

## **Background Document**

# **Clarifying the Scope of Petroleum Hazardous Waste Listings: Supplemental Information Regarding Petroleum Hydroprocessing Units**

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## Glossary and Acronyms

atm	Atmospheres (unit of measure for pressure)
Barrel	Equal to 42 gallons
BPSD	Barrels per Stream Day
CCR	Conradson Carbon Residue
Co	Cobalt
cSt	Centistokes
EP	End boiling point
EPA	U.S. Environmental Protection Agency
FCCU	Fluid catalytic cracking unit
Gravity, °API	Unit of measure for density of hydrocarbon fractions. A heavy liquid will have a low °API gravity.
H <sub>2</sub>	Hydrogen
HDN	Hydrodenitrogenation
HDS	Hydrodesulfurization
HDT	Hydrotreating
HDW	Hydrodewaxing
HVGO	Heavy vacuum gas oil
IP	Initial boiling point
K171	Spent hydrotreating catalyst from petroleum refining operations, including guard beds used to desulfurize feeds to other catalytic reactors (this listing does not include inert support material).
K172	Spent hydrorefining catalyst from petroleum refining operations, including guard beds used to desulfurize feeds to other catalytic reactors (this listing does not include inert support material).
LCO	Light Cycle Oil
LHSV	Liquid hourly space velocity. This is an indication of the flow velocity through the reactor. A relatively low number indicates relatively slow movement of hydrocarbon.
LPG	Liquid-Petroleum Gas
MHUG	Medium-Pressure Hydro Upgrading
Mo	Molybdenum
Naphtha	A light fraction used for gasoline production
Ni	Nickel. A catalyst ingredient and an impurity in hydrocarbon feedstock.
Nm <sup>3</sup> /m <sup>3</sup>	Normal cubic meter gas per cubic meter hydrocarbon feed. Normal conditions are 0°C and 1 bar pressure.
ppmw	parts per million by weight
PSA	Department of Energy's Petroleum Supply Annual
Resid	The heaviest fraction from atmospheric or vacuum distillation
scfb	Standard cubic feet of gas per barrel hydrocarbon feed. Standard conditions are 70°F and 1 atmosphere pressure.
UCO	Unconverted oil

## **Glossary and Acronyms (cont.)**

V	Vanadium
VGO	Vacuum gas oil
vol %	percent by volume
W	Tungsten
wt %	percent by weight

## 1. Introduction

On August 6, 1998, the Environmental Protection Agency (EPA) published final hazardous waste listing determinations for particular solid wastes generated at petroleum refineries (63 **FR** 42110). In that final rule, EPA listed spent hydrotreating catalysts (K171) and spent hydrotreating catalysts (K172) as hazardous wastes. (The final rule also included final listing determinations for several other petroleum refining wastes.) EPA took no action regarding a listing determination in the case of a third type of spent hydroprocessing catalyst, spent hydrocracking catalyst. However, the regulatory docket supporting the August 6, 1998 final rule did present available data characterizing spent hydrocracking catalysts in a Hazardous Waste Identification Study.<sup>1</sup>

Prior to publishing its final listing determinations for particular wastes generated at petroleum refineries, EPA collected a wide variety of facility- and waste-specific information relative to a number of different petroleum refining processes. Information collection activities included an industry survey and waste sampling and analyses. The listing determination decisions made by EPA and published on August 6, 1998, including the Agency's decisions to list spent hydrotreating and spent hydrotreating catalysts as hazardous waste, were based upon the results of these information collection activities. In the case of some refinery wastes, including spent hydrocracking catalysts, EPA presented available data without finalizing a regulatory determination.

The preamble to the August 1998 final rule provides definitions for three types of petroleum refinery hydroprocessing units from which spent catalysts may be generated and removed. The definitions are provided both to identify the two types of spent catalyst that are listed as hazardous waste and to aid in distinguishing spent hydrotreating and hydrotreating catalysts from spent hydrocracking catalysts. These definitions are based on the categories used in the Department of Energy's (DOE's) Petroleum Supply Annual (PSA) to differentiate between hydrocracking units and hydrotreating (treating/refining) units (63 **FR** 42155, August 6, 1998) for the purpose of reporting refinery production capacities to DOE. By the PSA's definition, catalytic hydrotreating is:

A refining process for treating petroleum fractions from atmospheric or vacuum distillation units (*e.g.*, naphthas, middle distillates, reformer feeds, residual fuel oil, and heavy gas oil) and other petroleum (*e.g.*, cat cracked naphtha, coker naphtha, gas oil, *etc.*) in the presence of catalysts and substantial quantities of hydrogen. Hydrotreating includes desulfurization, removal of substances (*e.g.*, nitrogen compounds) that deactivate catalysts, conversion of olefins to paraffins to reduce gum formation in gasoline, and other processes to upgrade the quality of the fractions.

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<sup>1</sup> U.S. EPA, Office of Solid Waste, "Study of Selected Petroleum Refining Residuals, Industry Study," August 1996 (EPA530-R-96-018).

In the 1998 final rule, EPA defined catalytic hydrotreating as a refining process similar to hydrotreating that uses higher temperatures and pressures than hydrotreating. The purpose of hydrotreating is to treat heavier molecular weight petroleum fractions (hydrotreating is not defined in the PSA). EPA also adopted the PSA definition of hydrocracking in the 1998 final rule. Catalytic hydrocracking is defined by the PSA as:

A refining process that uses hydrogen and catalysts with relatively low temperature and high pressures for converting middle boiling residual material to high-octane gasoline, reformer charge stock, jet fuel, and/or high grade fuel oil. The process uses one or more catalysts, depending upon product output, and can handle high sulfur feedstocks without prior desulfurization.

Although the preamble to the 1998 final rule referred to the general definitions used by DOE for the purposes of PSA reporting, the final rule did not include unit- or reactor-specific definitions or regulatory determinations for specific types of catalysts. When the final rule was published, EPA lacked information about certain types of hydroprocessing reactors may serve multiple functions. The Agency subsequently received inquiries regarding the regulatory status of spent catalysts removed from “dual purpose” reactors. Dual purpose petroleum hydroprocessing reactors are reactors that conduct hydrotreating (or hydrotreating) and hydrocracking in the same reactor.

In response to inquiries regarding the regulatory status of dual purpose hydroprocessing reactors, EPA issued guidance, in the form of two memoranda, clarifying that spent catalysts removed from dual purpose reactors are listed hazardous wastes. In a memorandum issued November 29, 1999, EPA stated that spent catalysts from petroleum hydroprocessing units performing hydrotreating or hydrotreating operations are listed hazardous wastes regardless of whether hydrocracking also occurs in the same reactor using a single catalyst. EPA clarified in the memorandum that the final rule defines a spent catalyst generated from a petroleum hydroprocessing reactor on the basis of the type of hydroprocessing operation in which the catalyst was used. If a spent catalyst is removed from a reactor that conducts hydrotreatment or hydrotreating, the spent catalyst is a listed hazardous waste. The memorandum further stated that refineries may not classify “dual purpose” reactors as hydrocracking reactors based solely on the fact that some hydrocracking takes place in the presence of the catalyst and then subsequently claim the spent catalyst to be non-hazardous.

In a second memorandum that was issued on June 1, 2000, EPA clarified that spent catalysts removed from hydroprocessing reactors that are designed primarily to hydrocrack previously treated petroleum feedstock, and that perform no more than minimal and incidental hydrotreatment are not listed hazardous wastes. EPA issued this second memorandum in response to concerns raised by the regulated community over the wording used in the November, 1999 memorandum. Members of the regulated community asserted that a strict reading of the November 1999 memorandum would render all spent catalysts from hydrocracking units as listed hazardous wastes due to the fact that some small amount of hydrotreating can occur in any hydrocracking reactor. As a result, the June 1, 2000 memorandum clarifies that spent catalysts from hydroprocessing reactors that perform a hydrocracking function (*i.e.*, hydrocrack previously

treated feed) and only a minimal and incidental hydrotreating function are not within the scope of the hazardous waste listing. In two letters written in response to specific questions posed by industry, EPA clarified the regulatory status of spent catalysts removed from two different types of hydroprocessing reactors. In the November 29, 1999 Memorandum and the subsequent memorandum and letters, EPA maintained that spent catalysts removed from dual purpose hydroprocessing units are listed hazardous wastes (K171 and K172).

In February 2000, API filed a lawsuit in the D.C. Circuit challenging the validity of the November 29, 1999 memorandum. *API v. EPA, Docket No. 00-1069*. In June 2001, API and EPA entered into a settlement agreement in regard to the second lawsuit. Under the terms of the settlement agreement EPA published a *Federal Register* notice (July 5, 2001; 66 *FR* 35379) announcing EPA's intention to accept comment on whether to maintain, and possibly clarify, the policy expressed in the memoranda regarding the regulatory status of spent dual purpose catalysts or to change it. After reviewing public comments received on the initial notice, EPA agreed to publish a second notice in the *Federal Register*.

This background document summarizes the results of a literature review and technical assessment identifying and characterizing petroleum hydroprocessing reactors, emphasizing dual purpose reactors. Three specific types of dual purpose reactors are identified and described. A summary of other types of petroleum hydroprocessing processes also is provided.

## **2. Overview of Hydrotreating, Hydrorefining, and Hydrocracking Processes**

The term hydroprocessing is used to denote processes by which molecules in petroleum feedstocks are split or saturated in the presence of hydrogen gas while reducing boiling ranges of and removing impurities from petroleum feedstocks. Hydroprocessing is a broad term that includes hydrocracking, hydrotreating, and hydrorefining. In addition to the terminology (presented above) that EPA used in the preamble to the 1998 final rule, the literature identifies specific characteristics for each type of process.<sup>2</sup> Reactions that take place during *hydrotreating* include the following (none greatly reduce the resulting molecular weight of the product) (Scherzer, 1996):

- Hydrodesulfurization (*i.e.*, the conversion of organo-sulfur compounds to H<sub>2</sub>S and similar weight organic compounds).
- Hydrodenitrogenation (*i.e.*, the conversion of organo-nitrogen compounds to NH<sub>3</sub> and similar weight organic compounds).
- Hydrodemetallation (*i.e.*, the precipitation of metal on catalyst in sulfide form).
- Hydrodeoxygenation (*i.e.*, the removal of -OH from molecule).
- Olefin hydrogenation (*i.e.*, the hydrogenation of olefins to aliphatic compounds).

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<sup>2</sup> The literature generally does not use the term hydrorefining. In general the characteristics of hydrotreating identified below are also applicable to hydrorefining.

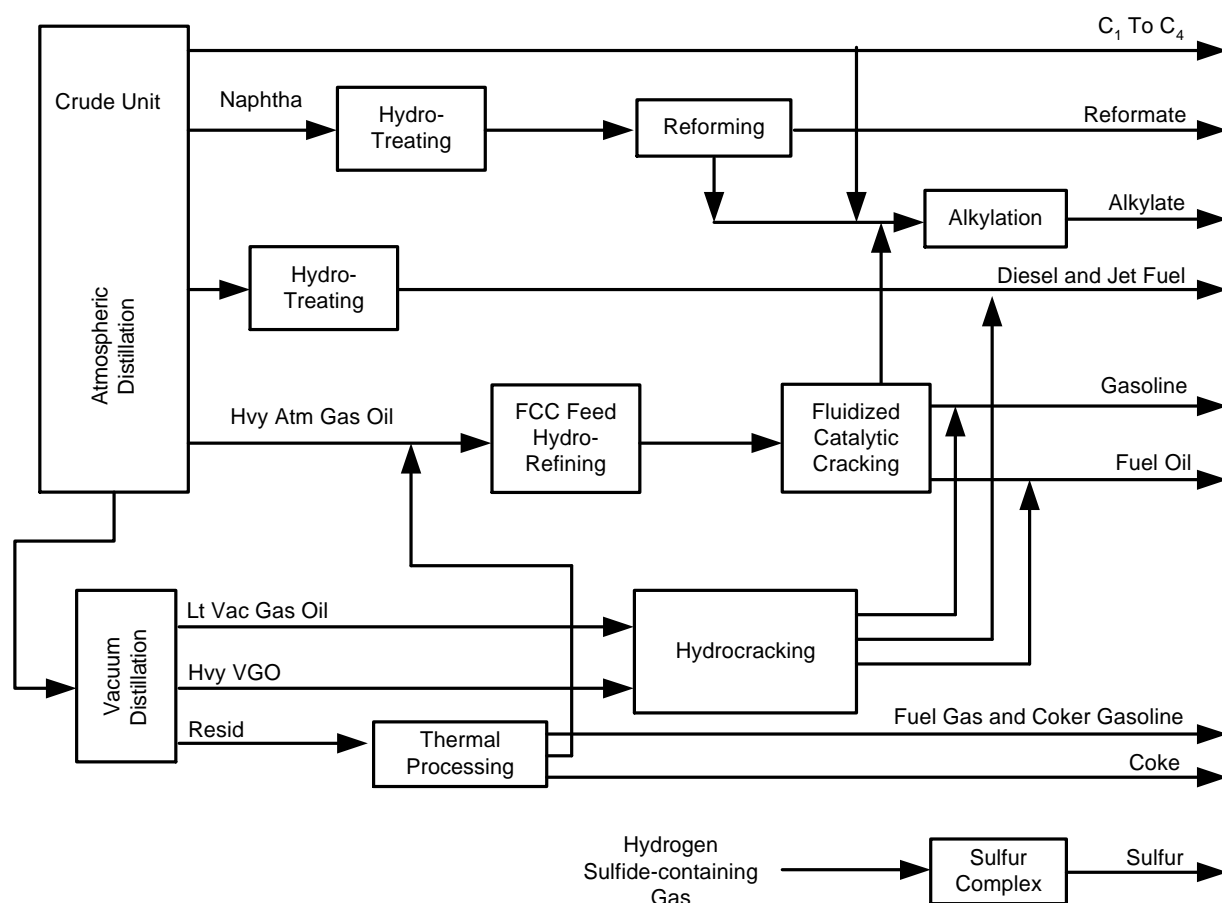
The PSA definition of hydrotreating (as cited in the preamble of EPA's August 1998 final rule) identifies sulfur, nitrogen, and other impurity removal as characteristics relevant to hydrotreating units. As a result, data on sulfur, nitrogen, and metals feed concentrations, and reactor-specific removal efficiencies, are presented in the following sections as available; such data are generally presented near the top of tables. However, other characteristics of hydrotreating units identified from the PSA definition (*e.g.*, olefin conversion) generally were found not to be well documented in the open literature, and therefore generally do not appear in the tables provided below.

Reactions that take place during *hydrocracking* include the following (Scherzer, 1996):

- Monoaromatics hydrogenation (*i.e.*, hydrogenation of phenyl rings).
- Hydrodealkylation (*i.e.*, the separation of aliphatic chain from phenyl ring).
- Hydrodecyclization (*i.e.*, breaking of saturated ring compounds).
- Isomerization of paraffins (*i.e.*, molecular rearrangement of aliphatic compounds).

Polyaromatics hydrogenation (*i.e.*, the saturation of polycyclic aromatic compounds) takes place during both *hydrocracking and hydrotreating*.

Figure 2-1 presents a flow diagram of a refinery; this diagram is intended to show approximately where hydroprocessing occurs in a refinery. Streams that undergo hydroprocessing include resid, naphtha, diesel, and lube oil.



**Figure 2-1. Typical Petroleum Refining Process Flow Diagram**

The different types of streams that can undergo hydroprocessing range from heavy feedstocks of resid and vacuum gas oil to lighter feedstocks of naphtha and distillate. Naphtha, or gasoline, is hydroprocessed to remove contaminants such as sulfur, which is harmful to downstream operations (such as precious metal reforming catalyst). Diesel hydroprocessing removes sulfur to meet fuel requirements, and saturates aromatics. The purpose of resid and VGO hydroprocessing is to remove metals, sulfur, and nitrogen (*e.g.*, *hydrotreating*), as well as to convert high molecular weight hydrocarbons into lower molecular weight hydrocarbons (*e.g.*, *hydrocracking*).

Several different types of heavy end hydroprocessing include hydrotreating, mild hydrocracking, high pressure hydrocracking, and medium pressure hydrocracking; all can be used with essentially similar feeds but with major differences in product quality. Mild hydrocracking operates at relatively low pressure (30–60 atm) to achieve partial conversion of feedstocks (*i.e.*, where the majority of the feed is not converted to lighter components). High pressure hydrocracking achieves high conversion of pretreated feeds (90 to 100 percent) using a combination of catalysts at high pressure (100 to 130 atm). As the name suggests, medium

pressure hydrocracking has operating parameters and product characteristics between mild and high pressure hydrocracking (Marion, 1998).

Data regarding the prevalency of hydroprocessing operations in U.S. refineries are provided in Table 2-1.

**Table 2–1. Population of U.S. Hydroprocessing Units**

<b>Process Type</b>	<b>Total Capacity, BPSD</b>	<b>No. of Refineries with Process <sup>2</sup></b>
Heavy Gas Oil Hydrotreating	2,316,160	54
Naphtha Reformer Feed Hydrotreating	4,276,664	120
Distillate Hydrotreating	3,942,220	101
Other/Residual Hydrotreating	904,660	41
Hydrocracking	1,575,800	42
Total U.S. Distillation <sup>1</sup>	17,393,070	158

Source: U.S. Department of Energy, 2000. Data do not include Puerto Rico and U.S. Virgin Islands.

1. Presented for context; includes refineries with and without hydroprocessing capacity.
2. A single refinery may have more than one unit within each process type.

Petroleum hydroprocessing reactors use catalysts to assist with chemical reactions necessary to remove sulfur and metals from feedstocks and reduce the boiling range of the feed. Amorphous and zeolite-based catalysts generally are used in hydrocracking reactors. The zeolite-based catalysts are high activity catalysts with high ammonia tolerance, and offer higher gasoline selectivity than do amorphous catalysts. Zeolites are microporous, crystalline aluminosilicates with ion exchange, sorption, and molecular sieving properties. Most zeolites are synthesized from a mixture of silica and alumina sources and caustic. Active catalysts are obtained by modifying the synthesized zeolite with ionic exchange and thermal or chemical treatment. High zeolite content catalysts rely primarily on the zeolite for their hydrocracking function. In low zeolite content catalysts, both the zeolite and acidic amorphous content are responsible for the cracking activity. Zeolite-based hydrocracking catalysts have certain advantages over amorphous catalysts such as greater acidity which results in greater cracking activity. They also possess better thermal/hydrothermal stability, naphtha selectivity, and resistance to nitrogen and sulfur compounds than amorphous catalysts. In addition to these advantages, the zeolite-based catalysts also have a low coke-forming tendency and can be more easily regenerated (Scherzer, 1996, p.15).

Catalysts used in hydrotreating reactors include cobalt and molybdenum oxides on alumina, nickel oxide, nickel thiomolybdate, tungsten and nickel sulfides, and vanadium oxide. Cobalt-molybdenum and nickel-molybdenum are the most commonly used catalysts for hydrotreating. Both types of catalyst remove sulfur, nitrogen and other contaminants from

petroleum feed. Cobalt-molybdenum catalysts, however, are selective for sulfur removal, while nickel-molybdenum catalysts are selective for nitrogen removal. (Gary, 1994, p.189)

Initial, or “guard,” reactors can be placed in front of hydrocracking reactors to remove contaminants, particularly metals, prior to hydrocracking. Guard reactors may employ a very inexpensive catalyst (five percent of the cost of CoMo catalyst) to remove metals from expanded bed feed. Spent demetallization catalyst can be loaded to more than 30 percent vanadium. A catalyst support having large pores preferentially demetallizes with a low degree of desulfurization. The opposite is true of catalyst supports having small pores (McKetta, 1992, p. 688-689).

### **3. Ebullated Bed (Dual Purpose) Processes**

Catalyst beds within petroleum hydroprocessing units may be fixed or moving. Most hydroprocessing reactors are fixed-bed reactors. Hydroprocessing units with fixed-bed reactors must be shut down to remove the spent catalyst when catalyst activity declines below an acceptable level (due to the accumulation of coke, metals, and other contaminants). There are a few types of hydroprocessing reactors with moving, or ebulating catalyst beds. In ebullated bed hydroprocessing, the catalyst within the reactor bed is not fixed. In such a process, the hydrocarbon feed stream enters the bottom of the reactor and flows upward through the catalyst; the catalyst is kept in suspension by the pressure of the fluid feed. Ebullating bed reactors are capable of converting the most problematic feeds, such as atmospheric resids, vacuum resids, and heavy oils (all of which have a high content of asphaltenes, metals, sulfur, and sediments) to lighter, more valuable products while simultaneously removing contaminants. The function of the catalyst is to remove contaminants such as sulfur and nitrogen heteroatoms, which accelerate the deactivation of the catalyst, while cracking (converting) the feed to lighter products. Because ebullating bed reactors perform both hydrotreating and hydrocracking functions, EPA also refers to them as dual purpose reactors. Ebullating bed catalysts are made of pellets that are less than one millimeter in size to facilitate suspension by the liquid phase in the reactor (Generalizations from: Scherzer, 1996; Gary, 1994; Colyar, 1997).

Licensed ebullating bed processes include:

- LC-Fining. Licensed by ABB Lummus Global Inc., Oxy Research and Development Co., and BP Amoco Corporation.
- H-Oil. Licensed by IFP North America and Texaco.
- T-Star. Licensed by IFP North America and Texaco.

LC-Fining and H-Oil both use similar technologies but offer different mechanical designs.

#### **3.1 H-Oil**

H-Oil is used to convert resid and heavy oils to upgraded petroleum products such as LPG, gasoline, middle distillates, gas oil, and desulfurized fuel oil. Stable operation is achieved through a high operating pressure which ensures a sufficient reactor outlet hydrogen partial

pressure. Typical operating conditions for the H-Oil process are shown in Table 3–1 (Colyar, 1997).

**Table 3–1. Typical H-Oil Process Operating Conditions**

Parameter	Value
Temperature, °C	415–440
Pressure, atm	168–207
LHSV, h <sup>-1</sup>	0.4–1.3
Catalyst Replacement Rate, kg/ton feed <sup>1</sup>	0.3–2.0
Single Train Throughput, bpsd	up to 34,000

Source: Colyar, 1997.

1. For a 40,000 BPSD design, this removal rate results in the generation of 2 to 13 tons of spent catalyst per day.

Tables 3-2 and 3-3 present performance data for H-Oil operation. Typical process performances for two different catalysts are shown in Table 3–2 for two-stage operation (in two-stage operation, two H-Oil reactors are used in series). Other catalysts are available, for example a different second generation catalyst achieving conversions greater than 80 percent (Colyar, 1997). Table 3–2 shows that sulfur, nitrogen, and metals are reduced between the feed and the product (up to 92 percent for sulfur, 50 percent for nitrogen, and 90 percent for metals), and that conversion up to 90 percent is achieved.

The H-Oil reactor is flexible in that it can handle feedstock with either high or low metals concentrations, although it is particularly efficient in treating and cracking heavier feedstocks (*e.g.*, vacuum resid). Table 3-3 shows intermediate product yields from two-stage H-Oil processing of vacuum resid from Arabian Medium crude at two conversion rates, 65 percent and 90 percent (Hydrocarbon Processing, 1998). Although typical nickel and vanadium concentrations of Arabian Medium crude are not particularly high (9.5 and 46 ppm, respectively; Environment Technology Center, 2000), the vacuum resid derived from the crude will have higher concentrations of these metals because metal compounds accumulate in the heavier fractions. The H-Oil reactor is designed particularly for the processing of these heavier fractions. Table 3-3 also shows the high desulfurization rates that can be achieved in an H-Oil reactor.

**Table 3–2. H-Oil Process Performance**

<b>Parameter</b>	<b>Results</b>	
	<b>1<sup>st</sup> Generation Catalyst</b>	<b>2<sup>nd</sup> Generation Catalyst</b>
Hydrodesulfurization, wt%	55–80	75–92
Nitrogen Removal, wt%	25–35	30–50
Metals Removal, wt%	65–90 (similar for each)	
Residue Conversion, vol%	45–90	45–85
CCR Conversion, wt%	45–65	65–75
H <sub>2</sub> Consumption, Nm <sup>3</sup> /m <sup>3</sup>	130–300 (similar for each)	

Source: Colyar, 1997. The 1<sup>st</sup> Generation catalyst is the standard catalyst. The 2<sup>nd</sup> Generation Catalyst is a new catalyst available for the H-Oil Process which is claimed to result in higher process performance and improved product quality affecting both the H-Oil distillates and unconverted residue.

**Table 3–3. Yields and Operation for Two-stage H-Oil Processing of Arabian Medium Vacuum Resid**

<b>Parameter</b>	<b>Product Results</b>	
	<b>65 % Conversion</b>	<b>90 % Conversion</b>
<i>Removal Rates</i>		
Desulfurization, wt % removal	91	84
CCR Conversion, wt % removal	69	82
<i>Yields</i>		
H <sub>2</sub> S & NH <sub>3</sub> , wt %	5.6	5.1
C <sub>1</sub> to C <sub>3</sub> , wt %	3.1	6.7
C <sub>4</sub> to 221°C, vol %	17.6	23.8
205°C to 371°C, vol %	22.1	36.5
371°C to 566°C, vol %	34.0	37.1
566 °C <sup>+</sup> , vol %	33.2	9.5
<i>Operating Parameters</i>		
H <sub>2</sub> consumption, scfb	1,410	1,860

Source: Hydrocarbon Processing, 1998.

Table 3–4 summarizes the feed properties and operating data for the H-Oil processing of vacuum resid derived from Arabian Heavy crude at two different conversion rates, 65 percent and 85 percent conversion. Again, the heaviest feedstocks (*e.g.*, vacuum resids) generally are found to contain the highest concentration of metals (Nongbri, 1992). The following conclusions are evident from Table 3-4:

- High levels of sulfur and nitrogen removal (90 percent and 66 percent, respectively), similar to the previous table.
- High levels of nickel and vanadium removal (81 percent and 91 percent, respectively).
- High, but not complete, conversion (up to 85 percent).
- Higher conversions of the feedstock result in slightly lower levels of desulfurization and metal removal.

**Table 3–4. H-Oil Processing of Arabian Heavy Resid**

Parameter	Feed Properties	Reduction (%) in Product	
		65% Conversion	85% Conversion
Sulfur, wt%	6.00	90.1	88.0
Nitrogen, ppmw	4,800	57.3	65.7
Nickel, ppmw	64	81.2	78.4
Vanadium, ppmw	205	91.4	88.4
538°C+, vol%	95.0	65.0	85.0
CCR, wt%	27.7	69.3	75.3
Hydrogen, wt%	9.86	—	—
Gravity, °API	3.0	—	—
Carbon, wt%	83.63	—	—
Hydrogen Consumption, scfb		1,550	2,440
Number of Stages		2	2

Source: Nongbri, 1992.

Tables 3-5 and 3-6 present sulfur content data for products resulting from the H-Oil process. Table 3-5 presents data from a Russian vacuum resid for a two-stage H-Oil process (where the two reactors are in series), operating at 68 volume percent conversion (Colyar, 1997). Table 3–6 presents typical product qualities obtained from a Heavy Arabian crude using the H-Oil process (Scherzer, 1996). Colyar (1997) identified the H-Oil process as demonstrating good selectivity to middle distillates and vacuum gas oil. Higher conversion rates show an increase in the selectivity towards lighter products including light gases. The unconverted resid can be used

as feed to a resid FCC Unit, or for other uses. Both tables demonstrate that the sulfur content of the products decrease as the products become ‘lighter.’ Additionally, the data in Table 3-6 show that the sulfur content of all products (including the heaviest) exiting the H-Oil unit are less than the concentration in the crude oil (note that the sulfur content of the actual feed to the H-Oil is most likely even greater than the sulfur content of the crude, because the feed to the unit is heavier than the crude).

**Table 3–5. Typical H-Oil Process Results**

Fraction	Yield, wt%	Yield, vol%	Sulfur, %
C <sub>1</sub> –C <sub>4</sub>	3.5	—	—
C <sub>5</sub> –180°C	6.3	8.7	< 0.01
180–370°C	25.5	29.8	0.05
370–538°C	33.9	36.3	0.21
538°C–	28.8	28.9	0.91

Source: Colyar, 1997. Two-stage H-Oil process using vacuum resid as feed, operating at 68 volume percent conversion.

**Table 3–6. H-Oil Processing of Arabian Crude: Typical Product Properties**

Fraction/Property	Virgin Crude	H-Oil Products		
		Naphtha	Middle distillate	Vacuum gas oil
Sulfur, wt %	2.7	0.06–0.15	0.26–0.59	0.71–1.55
Gravity, °API	22.5	62.0–62.2	34.4–34.5	16.4–19.8

Source: Scherzer, 1996. Table 14.10. Low conversion 70%. High conversion 90%.

Tables 3-7 and 3-8 present data regarding the metals content of feedstock to the H-Oil process. Nickel and vanadium are the two metals most often presented in the literature as typical feed contaminants. These two metals generally appear at higher concentrations than other metals in crude oil and can have deleterious effects on certain catalysts and fuel products.

Table 3-7 compares the products obtained from two different conversion rates, 65 volume percent and 85 volume percent, for a vacuum residue (38,000 bpsd of a nominal 565°C vacuum residue was processed). The feedstock is Arab Light/Heavy vacuum residue obtained from a 50/50 blend of Arabian Light and Heavy crudes, and is a standard for many company studies. The H-Oil process consisted of a single train with two H-Oil reactors in series. Table 3–7 illustrates the feed characteristics and product quality as a measure of sulfur content (Wisdom, 1997). Table 3–7 shows that the sulfur content of products exiting the H-Oil reactor is less than the sulfur content of the feed. However, there is a tradeoff between conversion and sulfur content: a higher conversion results in lower sulfur removal (*i.e.*, greater sulfur concentrations reside in the products as conversion increases). The relatively high nickel and vanadium feed concentration is demonstrative of the H-Oil unit’s capability to process feeds with high metal concentrations.

Table 3-8 presents characteristics of a vacuum resid (nominal 565°C) derived from a 60/40 blend of Isthmus and Maya crude processed in an H-Oil reactor (Wisdom, 1997). As above, the H-Oil process to which the vacuum resid was fed consisted of a single train with two H-Oil reactors in series operated at 38,000 bpsd. The feed had a sulfur content of 4.71 percent and a metals concentration of 707 ppmw. Other feed properties are identified in Table 3–8. The H-Oil product fractionator bottoms (expected to have the highest sulfur content of any fraction) had a sulfur content of 1.0 percent at moderate conversion (65 volume percent) and a sulfur content of 1.5 percent at high conversion (85 volume percent). These results demonstrate the treatment capability of the H-Oil reactor. As in the previous table, the high metal concentration of the feed is indicative of the H-Oil unit’s processing capabilities.

**Table 3–7. Product Quality for H-Oil Conversion of Arab Light/Heavy Vacuum Residue**

Parameter	Value
<i>Feed</i>	
Sulfur, wt%	5.33
Nickel + Vanadium, ppmw	221
Gravity, °API	4.7
CCR, wt%	24.6
<i>Sulfur Content of Products, wt%</i>	
Naphtha (moderately high conversion)	0.02
Mid-distillate (moderate conversion)	0.90
Mid-distillate (high conversion)	0.20
Vacuum Gas Oil (moderate conversion)	0.23
Vacuum Gas Oil (high conversion)	1.04

Source: Wisdom, 1997. Moderate conversion: 65%; High conversion: 85%.

**Table 3–8. Feedstock Inspections for Isthmus/Maya Feed**

<b>Parameter</b>	<b>Value</b>
Sulfur, wt%	4.71
Nickel + Vanadium, ppmw	707
Specific Gravity	1.06
Gravity, °API	1.5
CCR, wt%	27.8

Source: Wisdom, 1997.

### 3.2 LC-Fining

The LC-Fining ebullated bed process can achieve desulfurization, demetallization, CCR reduction, and hydrocracking of atmospheric and vacuum resids. This process yields a full range of high quality distillates; heavy residuals can be used as fuel oil, synthetic crude, or feedstock for a resid FCC, coker, visbreaker or solvent deasphalter. Operating conditions for the LC-Fining process include reactor temperatures of 385°C to 450°C and H<sub>2</sub> partial pressure of 68 to 184 atm. These can be compared to the H-Oil operating conditions in Table 3–1. The LC-Fining process can achieve conversion of 40 to 97 percent (or more), desulfurization of 60 to 90 percent, demetallization of 50 to 98 percent, and CCR reduction of 35 to 80 percent. Table 3–9 illustrates typical properties of Arabian Heavy/Arabian Light blends fed to the LC-Fining Process (Hydrocarbon Processing, 1998).

**Table 3–9. Typical Properties of LC-Fining Process Feedstock**

<b>Parameter</b>	<b>Value</b>	
	<b>Atm. Resid</b>	<b>Vac. Resid</b>
Sulfur, wt %	3.90	4.97
Ni/V, ppmw	18/65	39/142
Gravity, °API	12.40	4.73

Source: Hydrocarbon Processing, 1998. Blend of Arabian heavy and light.

### 3.3 T-Star

The T-Star process is a third ebullated bed process. T-Star units can maintain conversions in the range of 20 to 60 percent and hydrodesulfurization in the 93 to 99 percent range for four-year run lengths (Hydrocarbon Processing, 2000). The unit can act as either an FCCU pretreater or VGO hydrocracker. H-Oil catalyst can be used in the T-Star process. A T-Star reactor can also be placed in-line with an H-Oil reactor to improve the quality of H-Oil

distillate products such as virgin distillates, FCCU light or heavy cycle gas oil, and coker gas oils.

In mild hydrocracking mode, the T-Star process can reach conversions up to the 60 volume percent range. An advantage of operating the T-Star unit in mild hydrocracking mode is that the T-Star catalyst is not sensitive to sulfur and nitrogen levels in the feed and will provide constant conversion, product yields, and product quality. This consistency in output is due to the reactor catalyst being replaced while the unit remains on-line. A commercial scale demonstration of the T-Star Process in conjunction with the startup of H-Oil units was done as a joint venture between Husky Oil, Canada and HRI (HRI currently is IFP). The feed properties and process performance for the T-Star process are shown in Tables 3–10 and 3–11 (Johns, 1993). Table 3-10 shows that high levels of sulfur and nitrogen may be present in the feed to the T-Star unit. Table 3-11 shows that high percentages of sulfur and nitrogen are removed from the products as a result of T-Star processing.

**Table 3–10. Husky Oil Trial Feed Properties for T-Star Reactor**

<b>Parameter</b>	<b>Value</b>
Sulfur, wt%	2.8
Nitrogen, ppmw	1,328
Carbon Residue, wt%	0.21

Source: Johns, 1993.

**Table 3–11. T-Star Commercial Demonstration**

<b>Parameter</b>	<b>Results</b>
Hydrodesulfurization, wt %	91.7
Nitrogen removal, wt %	80.0
343°C+ Net Conversion, vol% <sup>1</sup>	9
Hydrogen Consumption, scfb	642

Source: Johns, 1993.

1. Examples of products lighter than 343°C include light naphtha, heavy naphtha, and light gas oil. An example of a product heavier than 343°C is heavy gas oil.

Tables 3-12 and 3-13 show, respectively, the properties of a feedstock processed in the T-Star process and the resulting product qualities. The T-Star process was operated at a conversion rate of 30 percent and was used to produce FCC unit feed from a single stage operation using a single catalyst system under moderate pressure levels (Nongbri, 1996). The predominant

feedstock was vacuum gas oil that was not treated prior to being fed to the T-Star reactor. Table 3-12 shows that, in this case, the sulfur and nitrogen levels of the feed are relatively high. Table 3-13 shows that the sulfur and nitrogen levels of the products (including the heaviest products) are lower than the feed levels as a result of T-Star processing.

**Table 3–12. T-Star Reactor Feedstock Components and Properties**

Parameter	Value
Sulfur, wt %	1.93
Total Nitrogen, ppmw	1820
Nickel, ppmw	1.6
Vanadium, ppmw	4.4
Watson Aromatics, wt %	61.7
Gravity, °API	23.7
182°C and lighter, wt %	4.0
182–360°C, wt %	23.4
360°C+, wt %	72.6
Feed components: Virgin Vacuum Gas Oil (71%), Coker Light Gas Oil (9%), Aromatic Extracts (9%), Coker Heavy Gas Oil (6%), and Heavy Coker Naphtha (5%)	

Source: Nongbri, 1996.

**Table 3–13. T-Star FCCU Feed Yields at 30 Percent Conversion**

Feed or Product Fraction	Gravity, °API	Sulfur, wt %	Nitrogen, ppmw
Feed property (from previous table)	23.7	1.93	1,820
<u>Product Fraction</u>			
H <sub>2</sub> S and NH <sub>3</sub>	—	—	—
C <sub>1</sub> – C <sub>4</sub>	—	—	—
C <sub>5</sub> – 65°C	85.6	0.007	—
65 – 170°C	59.0	0.007	3
170 – 360°C	33.7	0.009	46
360°C +	25.5	0.100	766
Overall Reduction Rate	—	97 wt% reduction	78 wt% reduction

Source: Nongbri, 1996. Hydrogen consumption is 700 SCFB.

Tables 3-14 and 3-15 present data for the T-Star process operating in mild hydrocracking mode using a single stage operation and a single catalyst system under moderate pressure levels

(Nongbri, 1996). The T-Star process was operated at a conversion rate of 55 percent; Table 3-14 shows that, in this case, the predominant feedstock was vacuum gas oil without any type of prior processing; as a result the sulfur and nitrogen levels of the feed are relatively high. Table 3-15 shows that the sulfur and nitrogen levels of the products (including the heaviest products) are lower than the feed levels as a result of T-Star processing.

Tables 3-12 to 3-15 show that desulfurization was in excess of 97 percent for each operation of the T-Star reactor. For the two operations identified, denitrogenation was 78 percent in the first case and 94 percent in the second (Nongbri, 1996).

**Table 3–14. T-Star Reactor Feedstock Properties**

Parameter	Value
Gravity, °API	23.5
Sulfur, wt %	2.10
Total Nitrogen, ppmw	819
Watson Aromatics, wt %	54.2
Nickel, ppmw	<5
Vanadium, ppmw	<5
182°C and lighter, wt %	0
182–360 °C, wt %	29.0
360°C+, wt %	71.0
Feed components: Virgin Vacuum gas Oil (75%), Light Cycle Oil (13%), Virgin Diesel (12%)	

Source: Nongbri, 1996.

**Table 3–15. T-Star Mild Hydrocracking Yields at 55 Percent Conversion**

Feed or Product	Gravity, °API	Sulfur, wt %	Nitrogen, ppmw
Feed property (from previous table)	23.5	2.10	819
<u>Product Fraction</u>			
H <sub>2</sub> S and NH <sub>3</sub>	—	—	—
C <sub>1</sub> – C <sub>4</sub>	—	—	—
C <sub>5</sub> – 65°C	90.0	0.01	1
65 – 170°C	57.5	0.02	4
170 – 360°C	35.0	0.03	30
360°C+	32.2	0.08	90
<b>Overall Reduction Rate</b>	—	98 wt% reduction	94 wt% reduction

Source: Nongbri, 1996. Hydrogen consumption is 922 scfb.

### 3.4 Population

EPA is aware of two facilities in the U.S. that use ebullated bed technologies. These facilities are identified in Table 3–16. The two facilities were identified in an evaluation of data collected for EPA’s 1992 petroleum refining survey. The data in Table 3–16 do not include facilities which may have constructed new units after 1992 (the year for which EPA’s data were collected), or which were otherwise not identified from EPA’s data.

**Table 3–16. Summary of U.S. Refineries Using Ebullated Bed Technology**

<b>Refinery Name</b>	<b>Licensor and Name of Hydroprocessing Unit</b>	<b>Capacity, BPSD</b>	<b>Catalyst Type</b>
BP Amoco, Texas City TX	C. E. Lummus LC-Fining	75,000	No data
Motiva, Convent LA	Texaco H-Oil	40,158	Ni/Mo

Source: Non-CBI data from the database developed from the 1992 EPA petroleum refining solid waste survey.

### 3.5 Conclusions

Based on the data presented in this section, the following conclusions are evident regarding ebullated bed processes:

- There are three different licensed ebullated bed processes: H-Oil, LC-Fining, and T-Star. In each of these processes, the ebullated bed operates so that there is constant withdrawal and replacement of the catalyst.
- Ebullated bed processes use very heavy feeds such as vacuum gas oil or vacuum residue. Such feeds have correspondingly elevated sulfur, nitrogen, and metals content (*i.e.*, compared to other crude oil distillation cuts). The feeds are not pretreated prior to the ebullated bed process.
- Ebullating bed processes yield high product conversions, however the conversion is not 100 percent.
- High sulfur reduction is seen in all products. Nitrogen is also significantly reduced, but to a lesser degree than the sulfur.
- The process can accept feedstocks with elevated metals content (*e.g.*, up to 700 ppm in one case); the metals content of each product is less than the feed concentration indicating that the unit is hydrotreating the feed.

#### 4. Mild Hydrocracking

The purpose of mild hydrocracking is to convert vacuum gas oil to low sulfur distillates at operating conditions consistent with those for hydrotreating equipment. Full conversion of the feedstock does not occur in the mild hydrocracking process. Typically the process yields conversions of 20 to 60 percent (Marion, 1998). The products obtained through mild hydrocracking are high quality, low sulfur/nitrogen diesel and unconverted VGO fractions. The VGO fraction is desirable as FCC feedstock due to its high hydrogen content and reduced sulfur and nitrogen levels. The product properties of the fractions depends on the feedstock characteristics and the process operating conditions (Johns, 1996).

Most often, mild hydrocracking units are re-designs of existing hydrotreating VGO process units. The process employs a single reactor and operates on a once-through basis, designed to partially convert the VGO into low-sulfur naphtha or distillate. The feed to a mild hydrocracking unit is mostly vacuum gas oil but can also be other heavy feedstock (Scherzer, 1996). Catalysts used in this type of unit are multi-purpose in that they perform the hydrotreating functions of desulfurization and denitrogenation but also convert the heavy fuel oil molecules into lighter mid-distillates (Desai, undated). The catalysts are mildly acidic, usually consisting of cobalt or nickel oxide combined with molybdenum or tungsten oxide, supported on amorphous silica-alumina or mildly acidic zeolite (Scherzer, 1996).

The process operates under temperature conditions of 350–440°C and pressures of 30–100 atm (Scherzer, 1996). The hydrogen partial pressure has the greatest effect on the mild hydrocracking process. Higher pressures result in higher reaction rates and increased catalyst stability. Lower pressures facilitate deactivation of the catalyst due to the fact that the reactive coke precursors are not hydrogenated quickly enough to prevent coke formation on the catalyst. Reactor pressure cannot always be controlled, however. Instead, it is dependent on the available pressure of the hydrogen gas, which would otherwise require installation of costly compressors to increase pressure. To compensate for varying pressures, the reactor temperature can be adjusted to achieve similar results (Johns, 1996).

Table 4–1 shows typical feed properties for a mild hydrocracking process. The metal concentration of less than 20 ppmw is significantly less than the typical metal concentration of an ebullating bed feedstock. The sulfur and nitrogen levels, however, are elevated. Table 4–2 shows typical unit performance and product yields and qualities of mild hydrocracking operated at 30 percent conversion (Marion, 1998). Table 4–2 shows high desulfurization rates for all products, including the heaviest fractions.

**Table 4–1. Typical Mild Hydrocracking Feedstock Characteristics**

<b>Parameter</b> <sup>1</sup>	<b>Value</b>
Gravity, °API	22.1
S (wt %)	2.7
N (ppmw)	800
Nickel (ppm) <sup>2</sup>	2.5
Vanadium (ppm) <sup>2</sup>	16
Boiling Point at 5 wt%, °C	370
Boiling Point at 50 wt%, °C	460
Boiling Point at 95 wt%, °C	550

Source: Marion, 1998 unless otherwise indicated.

1. Properties of vacuum gas oil (370 to 550°C) derived from Arabian light crude.

2. Source: Environment Technology Center 1996–2000.

**Table 4–2. Typical Mild Hydrocracking Performances Based on Arabian Light**

<b>Fraction</b>	<b>Yield</b>		<b>S, ppmw</b>	<b>Gravity °API</b>	<b>Polyaromatics, wt %</b>
	<b>Wt %</b>	<b>Vol %</b>			
Feed property (from previous table)	—	—	27,000	22.1	—
H <sub>2</sub> S + NH <sub>3</sub>	2.85	—	—	—	—
C <sub>1</sub> – C <sub>4</sub>	0.70	—	—	—	—
Naphtha	1.75	2.09	—	—	—
Diesel	25.23	26.71	300	—	<11
VGO Product	70.27	72.31	<1000	26.6	—
TOTAL	100.80	101.78	—	—	—

Source: Marion, 1998, p.52. Two year cycle length. Overall conversion: 30 wt %.

#### 4.1 MHUG

One mild hydrocracking processes is called MHUG (Medium-Pressure Hydro Upgrading) technology. It is presented by Technip Benelux in alliance with RIPP/Sinopec. The MHUG process uses medium-pressure, single-stage, once-through technology to produce low-sulfur, low-aromatics diesel or naphtha reformer feed. Feedstocks can range from light diesel-range feedstocks to heavy vacuum gas oil boiling-range fractions. This process operates at a pressure below 100 atm, has low operating temperatures and hydrogen consumption, and has a long

catalyst cycle time. This process has been used to revamp existing processes and has also been installed as a grassroots process (Chen, 1999).

The process is designed such that two catalysts are placed in series within a single reactor. The first catalyst (designated RN by the licensor) is a hydrotreating catalyst, while the second (designated RT by the licensor) is a mild hydrocracking catalyst. Both have Ni-W as an active component. The RN series catalysts are identified as having strong hydrodenitrification, hydrodesulfurization, and hydrodearomatisation functions. The RT series catalysts are designed to promote the partial saturation of polynuclear aromatics, the ring opening of naphthenic aromatics, and the ring opening of naphthenes (Chen, 1999).

Mild hydrocracking maintains the hydrotreating advantage of sulfur reduction while achieving significant conversion of the feed. Table 4–3 shows the pilot-plant test results for the mild hydrocracking of an FCC feedstock vacuum gas oil derived from a naphthenic type of crude oil at a conversion rate of 35 percent (Chen, 1999). The table demonstrates high rates of desulfurization and denitrogenation in each of the products.

**Table 4–3. Test Results for MHUG Application to Mild Hydrocracking of FCC Feed**

Parameter	Value in Feed	Value in Product		
		Naphtha	Diesel	Hydroconverted oil
Yield, wt %	—	7.15	26.81	64.51
Sulfur, ppmw	10,000	16	19	9
Nitrogen, ppmw	2,400	<0.5	<0.5	6
Initial boiling point, °C	251	—	180	—
50% Boiling Point, °C	447	—	—	—
Final boiling point, °C	503	—	350	—
Aromatics, wt %	39.3	56.3 (potential)	—	16.9
Hydrogen content, wt %	—	—	—	13.34

Source: Chen, 1999.

The MHUG process also can be used to upgrade light cycle oil (a lighter fraction than VGO) to low sulfur, low aromatics diesel fuel. The hydrodearomatisation function of the catalyst makes it an ideal process for upgrading LCO to a premium diesel component. This mode of operation typically operates under hydrogen partial pressures of around 65 atm and temperatures in the range of 350 to 365°C. If diesel is the desired product, a diesel yield of 95 percent is typical under these operating conditions. Table 4–4 illustrates the pilot plant test results for MHUG application to upgrade LCO (Chen, 1999). Table 4-4 identifies significant reductions in sulfur content, nitrogen content, and aromatics content from the feed to the diesel product.

**Table 4–4. Test Results of LCO Upgrading Using MHUG**

<b>Parameter</b>	<b>Value in Feed</b>	<b>Value in Product</b>	
		<b>Naphtha</b>	<b>Diesel</b>
Yield, wt %	—	7.0	93.0
Sulfur, ppmw	10,400	—	16
Nitrogen, ppmw	446	<0.5	1.4
Aromatics, vol %	48.2	—	17.8
Cetane Index	39.0	—	52.0
Initial Boiling Point, °C	203	—	—
50% Boiling Point, °C	279	—	—
Final Boiling Point, °C	360	—	—

Source: Chen, 1999.

#### 4.2 Population

From the information collected, it was not possible to estimate the population of mild hydrocracking facilities within the United States. Mild hydrocracking units are often re-designs of existing VGO hydrotreating process units; it is difficult to identify refineries who have conducted such changes.

#### 4.3 Conclusions

Based on the above information, the following conclusions are reached regarding mild hydrocracking processes:

- Mild hydrocracking processes use heavy feeds such as vacuum gas oil. Mild hydrocracking does not accept the heaviest refinery feeds such as those used for some ebullated bed processes. The feeds are not pretreated prior to the mild hydrocracking process.
- Facilities will often ‘retrofit’ an existing reactor to mild hydrocracking mode. For this reason it is difficult to estimate the population of facilities operating mild hydrocracking units.
- The process employs a single fixed bed reactor and operates on a once-through basis.

- Mild hydrocracking bed processes yield product conversions much lower than 100 percent. The heaviest product is used for FCC feed, fuel oil, *etc.*
- Mild hydrocracking reduces the sulfur and nitrogen heteroatom concentrations in all products. Reductions in aromatic content also were noted when mild hydrocracking was used for diesel fuel upgrading (Table 4-4).
- Limited data are available describing reductions in metals content achieved via mild hydrocracking processes. The data available indicate that feedstocks for mild hydrocracking processes generally have relatively low metals content. For example, the Arabian light crude from Table 4-1 has a total metals content of only 20 ppm. Data are insufficient to determine whether feedstocks with higher metals contents can be successfully processed, or if the metals in the feedstocks are deposited on the catalyst or “pass through” to the products. No data on metals removal percentages, or the metals content of products, were identified.

## 5. Single- and Multi-Stage Hydrocracking Processes

Several licensors provide staged hydrocracking technologies. Hydrocracking is typically classified as single-stage or two-stage unit operations. While nomenclature and design objectives differ for each licensor and application, several similarities are evident. These include the following:

- Catalysts are present within a fixed bed reactor, or series of reactors.
- Heavy feeds, such as vacuum gas oil, are typically processed.
- Lighter, more valuable products such as naphtha, jet fuel, and distillate are produced.
- Some or all of the heaviest product can be recycled to the reactors.
- Objectives typically include sulfur/nitrogen removal and conversion to lighter fuels. Such objectives often require the use of different types of catalysts at different points in the process.

In single-stage processing, one or more reactors are used. If one reactor is used, multiple catalysts can still be employed by using a stacked bed arrangement of different catalysts. Heavy hydrocarbon and hydrogen is fed to the first reactor that generates hydrogen sulfide and ammonia gases as a result of hydrodesulfurization and hydrodenitrification reactions. However there is no separation of products between the first and second reactors, so that the second reactor receives the gases and light products generated from the first reactor (George, 1994). Typically 40 to 80 percent of the feed volume is converted in one pass. If the fractionator bottoms are not recycled, higher conversion (90 percent) can be achieved with lower temperatures and lower hydrogen partial pressures (Scherzer, 1996).

In two-stage processing, light gases and relatively light petroleum products (such as naphtha) are removed between the two reactors. The remaining feed then proceeds to the second reactor (George, 1994). An advantage to this configuration is that better conversion (*i.e.*, cracking) results are achieved in the second reaction because the reaction occurs in the absence of

ammonia; ammonia inhibits the activity of hydrocracking catalyst (Criterion, 1998). A second advantage of two-stage operation is that the capacity of the second reactor is essentially increased: greater quantities of heavier feedstock can be fed to the second reactor as the light gases and products are separated from the feed after being treated in the first reactor. Table 5-1 illustrates typical operating conditions for conventional one or two-stage hydrocracking (Scherzer, 1996).

**Table 5-1. Single or Two-Stage Hydrocracking Operating Conditions**

Parameter	Value
Conversion, wt%	70-100
Temperature, °C	350-450
H <sub>2</sub> partial pressure, atm	100-200
LHSV, h <sup>-1</sup>	0.5-2.0
Hydrogen Feed Rate, Nm <sup>3</sup> /m <sup>3</sup>	1000-2000

Source: Scherzer, 1996 (Chapter 12).

In the case of most two-stage units, the different reactors have different functions. One way this is illustrated is through the type of catalyst(s) used in each reactor. For example, one catalyst can be designed for primarily sulfur and nitrogen reduction, and a second catalyst designed primarily for cracking. A single catalyst can have multiple effects, or a single reactor or series of reactors can contain multiple catalysts (as shown in the example presented in Section 5.2 below). In cases where multiple catalysts are used, the initial catalyst is used for (1) pretreating the feed to remove nitrogen and sulfur, and (2) aromatics saturation. These are followed by cracking catalysts which convert heavy oil to either gasoline or distillate fuels (Criterion, 1998). Criterion (1998) also describes post-treat catalysts that may be used to stabilize the product by preventing reactions between hydrogen sulfide and olefins that form mercaptans.

Guard reactors are used in hydrocracking processes to protect catalysts in subsequent reactors, including precious metals hydrocracking catalysts, from contaminants in feedstocks that are not previously hydrotreated. If a hydrocracking unit is designed to accept feedstocks that have not been hydrotreated previously, a guard reactor precedes the first hydrocracking reactor in the process flow. The purpose of the guard reactor is to convert organic sulfur and nitrogen compounds to hydrogen sulfide and ammonia. Guard reactors also serve the purpose of reducing the metals content in the feed to the hydrocracking units. Catalysts used in guard reactors are usually modified hydrotreating catalysts such as CoMo on silica-alumina. Most of the metals in the feed will be deposited on the catalyst in the guard reactor and there will be a substantial reduction in the Conradson and Ramsbottom carbons, resulting in a feed to the hydrocracking reactors that is low in metals and carbon forming precursors (Gary, 1994, p.156, 174-176).

An example of a two-stage hydrocracking unit, consisting of two separate reactors and a fractionator, was described for a Kuwait refinery (Maheshri, 2000). The feed is vacuum gas oil,

where some sulfur reduction has already taken place: crude unit residue is hydrotreated and fed to a vacuum rerun unit, where VGO is drawn off to become hydrocracking feed.<sup>3</sup> The two-stage hydrocracking unit normally is operated such that feed enters the first stage, light products and gas are removed, and the majority of the fractionator bottoms are continuously recycled to the second stage to achieve an overall conversion of 95 percent.

The MDQ Unionfining process is an example of a process that can be constructed as either a single or two-stage operation. Single-stage typically uses one or two reactors. These reactors use base-metal catalysts that may be the same or different for each reactor. The two-stage process uses noble-metal catalysts in the second-stage reactor where there is a much lower contaminant concentration due to interstage gas stripping (Heckel, 1998).

Licensed single- and two-stage hydrocracking units include:

- ? IFP Technology. IFP, North America.
- ? MAKFining. Licensed by Kellogg Brown & Root.
- ? Shell Hydrocracking Process, Shell International Oil Products B.V.

Examples of these processes are discussed in Sections 5.1, 5.2, and 5.3, respectively.

#### 5.1 IFP Technology Hydrocracking

IFP hydrocracking is used for the purpose of upgrading straight vacuum gas oil or VGO blended with LCO, deasphalted oil, visbreaker, or coker gas oil. Three different process arrangements are available: single-stage, single-stage with recycle, and two-stage hydrocracking. Organic heteroatom removal is a major part of single and two-stage hydrocracking. Therefore, in two-stage processing, this process uses a hydrotreating catalyst followed by a zeolite-type hydrocracking catalyst (Hydrocarbon Processing, November 2000). Table 5-2 demonstrates the sulfur and nitrogen reduction of a 50/50 Arabian light/heavy blend using IFP fixed-bed hydrocracking technology (Hydrocarbon Processing, November 1998). The data show that sulfur and nitrogen in the two products removed from the IFP hydrocracking unit are much lower than the feed levels. However, the data are incomplete because sulfur and nitrogen levels in the heaviest fraction (where the highest levels are expected) were not presented in the source literature.

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<sup>3</sup> A typical sulfur content of Kuwait crude is 2.52 percent (ETC, 2000). The sulfur content of the actual unit feed in this case may be higher or lower depending on the specific crude source, the degree that sulfur is 'concentrated' in the bottom fractions, and the severity of upstream desulfurization in this instance.

**Table 5-2. Sulfur and Nitrogen Reduction from IFP Hydrocracking Process**

Parameter	Feed HVGO (50/50 Arabian light/heavy)	Product	
		Jet Fuel	Diesel
Sulfur, ppm	31,700	<10	<20
Nitrogen, ppm	853	<5	<5
Metals	<sup>1</sup>	—	—

Source: Hydrocarbon Processing, November 1998.

1. The nickel and vanadium content of Arabian Light crude oil are 2.5 ppm and 16 ppm, respectively (Environment Canada 2000). The HVGO feedstock is expected to have higher levels of metals because it is derived from a blend of light and heavy crude (where the heavy crude is expected to have higher metals concentrations), and the VGO fraction is expected to concentrate these metals somewhat.

## 5.2 MAKFinining

The Kellogg MAKFinining process is capable of converting feedstocks such as vacuum gas oil, coker gas oils, and FCC cycle oils into high-quality, low-sulfur fuels. This process can be operated as a single-pass or extinction (*i.e.*, complete recycle of fractionator bottoms) process. Multi-bed reactors using multiple catalysts are used in this process (Hydrocarbon Processing, November 2000).

Table 5-3 shows the sulfur and nitrogen levels in the feed that can be processed using MAKfinining technology. This table was developed from operations where VGO derived from a 50/50 blend of Arabian light and heavy was processed in the MAKFinining unit. The sulfur content of the diesel product is reduced.

**Table 5-3. Sulfur and Nitrogen Reduction Through MAKFining Technology**

Parameter	Feed	Product			
		Naphtha	Kerosene	Diesel	Gas Oil
Sulfur, ppm	29,000	—	—	<50	—
Nitrogen, ppm	900	—	—	—	—
Yield, %	—	12.9-22.6	14.1-24.5	31.8-32.5	30-50
Operation mode	Single pass				
Temperature, °C	370-430				
Pressure, atm	70-140				

Source: Hydrocarbon Processing, November 1998.

Range: bound from low conversion (50%) to high conversion (70%). Higher conversion gives higher yields of lighter products.

One refinery in Austria converted its existing VGO HDS reactor into a two reactor system (using MAKFining Technology). The two reactors are in series, with no intermediate separation or fractionation, and would be considered a ‘single stage’ system according to the above terminology by George (1994). The unit is not designed to achieve complete conversion; only 33 percent conversion is achieved with the heavier product being fed to the FCC. The following catalysts were identified for use in the initial start-up in 1997 (Danzinger, 1999):

- For the first reactor, three catalysts were used together:
  - Akzo Nobel KF-647. An HVGO demetallization catalyst with high hydrodenitrogenation (HDN), hydrodesulfurization (HDS), and hydrogenation activity.
  - Akzo Nobel KF-840. A high activity catalyst for HDN
  - Akzo Nobel KF-901H. A Ni/Co/Mo catalyst with high HDS and HDN activity.
- For the second reactor, only one catalyst was used: Akzo Nobel KC-2602. A zeolytic Co/Mo catalyst combining hydrocracking activity for HGO conversion with high HDS performance.

These catalysts suggest that the first reactor is used to achieve nitrogen and sulfur removal. Sulfur removal also appears to be an objective of the second reactor, in addition to hydrocracking. Criterion (1998) also verifies that some two stage hydrocracking designs are exposed to elevated hydrogen sulfide levels in the second stage, but not to ammonia. Overall sulfur reduction (Danzinger, 1999) is from 0.63 wt percent to 0.0047 wt percent in the FCC feed; overall nitrogen reduction is from 1700 ppmw to 454 ppmw in the FCC feed. The first reactor temperature is 410°C and the inlet pressure is 71 atm. No data are available to identify differences in feed characteristics between the two reactors.

### 5.3 Shell Hydrocracking Process

The Shell hydrocracking process converts heavy VGO and other cracked and extracted feedstocks to products such as low-sulfur diesel and jet fuel, high-octane light gasoline, and reformer, cat cracker or lube oil feedstocks. The process can be either a single-stage or two-stage unit. A single reactor stacked catalyst bed is best suited for capacities up to 10,000 tons per day (about 65,000 barrels per day) in either partial or full conversion modes. In this process, heavy hydrocarbons are mixed with fresh hydrogen and passed through multi-bed reactor(s) which contain proprietary pre-treat, cracking, and post-treat catalysts (Hydrocarbon Processing, November 2000).

EPA visited one refinery with a two-stage hydrocracking process using Shell technology during its development of the 1995 proposed rule. This refinery (Equilon, formerly Shell, in Wood River Illinois) uses a two stage process, wherein the first stage catalyst conducts a hydrotreating function (Ni/Mo catalyst) and the second stage catalyst conducts a hydrocracking function (Ni/W on zeolite). Operating conditions of the second stage are 315 to 343°C, and approximately 125 atm (U.S. EPA, 1995).

### 5.4. Isocracking Technology

Chevron's Isocracking Technology is another example of a licensed hydrocracking process. Three options exist for the design of an Isocracking unit: single-stage once through (SSOT), single-stage recycle (SSREC), and two-stage. These options are very similar to those discussed above for stage hydrocracking processes in general.

The most common Isocracking unit configuration is the two-stage unit consisting of two reactor stages and a product distillation section. Generally, the first stage catalyst performs denitrification and desulfurization of the hydrogenated gas oil feed with minimal hydrocracking. Before the feed is sent to the second reactor stage, it is passed through a product fractionator which removes the conversion products of the first stage to avoid re cracking in the second stage. Hydrocracking of the feed occurs in the second stage reactor. The relatively low operating temperatures of this stage result in good selectivity and product quality. Complete conversion of the feed is accomplished by recycling all unconverted material back to the second stage reactor (Dahlberg, 1995).

An SSOT Isocracking unit is similar to the first stage of the two-stage process. In such a unit, the feedstock is not completely converted into lighter products. The typical product of this type of unit is a highly refined heavy oil (McKetta, 1992).

An SSREC Isocracking unit completely converts heavy oils to lighter products as in the second stage of the two-stage unit design (*i.e.*, where the heaviest fraction is recycled to the reactor) (McKetta, 1992).

Different catalysts are used in these units depending upon the feed available, products required, and the number of process stages in the design of the unit. Table 5-4 lists typical hydrocracking catalysts used in Isocracking process units (McKetta, 1992).

**Table 5-4. Typical Isocracking Catalysts**

Catalyst Number	Use in Isocracking Units	
	Single Stage Design	Two Stage Design
ICR 106 and ICR 120	High ratio of mid-distillate to naphtha	First stage denitrification and cracking Second stage hydrocracking for mid-distillate emphasis
ICR 113	Used for hydrocracking heavy oils like DAO	First stage denitrification
ICR 117	High ratio of naphtha to mid-distillate	First stage denitrification and cracking Second stage hydrocracking for naphtha and mid-distillate
ICR 201	Hydrocracking naphtha or raffinate to LPG	Second stage hydrocracking for LPG from naphtha or raffinate
ICR 202	—	Second stage hydrocracking for naphtha or jet fuel
ICR 204	—	Second stage hydrocracking for naphtha, aromatics, and jet fuel

Source: Chevron Research Co. From McKetta, 1992 (pg. 603).

As can be seen from this table, the same catalyst can perform different or multiple functions within an Isocracking unit, depending upon the process stage in which it is used. For example, Chevron's catalyst ICR 113 is used for hydrocracking heavy oils if used in a single-stage Isocracking unit. In such a unit the catalyst performs both the hydrotreating and hydrocracking functions. But its primary function, when used in the first stage of a two-stage Isocracking unit, is denitrification (a hydrotreating function). Therefore, the classification of a catalyst within an Isocracking unit as either hydrotreating or hydrocracking is dependent upon the function of the catalyst within a given process stage.

An example of Chevron's mild Isocracking catalyst system being used to upgrade an exiting process is at the Nippon Petroleum Refining Co.'s (NPRC) Muroran, Japan facility. The facility's hydroprocessing system originally was designed for desulfurization of Arabian VGO. In the early 1980's, Muroran shifted to severe desulfurization, using the existing hydrodesulfurization catalyst. Chevron's mild Isocracking catalyst system was installed in 1982, and the Muroran unit continues to operate in this mode (as of 1992). Table 5-5 provides a comparison of product yields and properties for three modes of operation for the Isocracking system yielding Isomate distillates. The light Isomate distillate product meets Japanese diesel specifications for sulfur, cetane index, pour point, and distillation and the heavy Isomate bottoms product is used as a fuel oil blend stock or FCC feed. The nitrogen reduction achieved in the

Isocracking system leads to improved FCC catalyst activity, conversion, and yields (McKetta, 1992).

**Table 5-5. Feed and Product Data for Isocracking**

<b>Parameter</b>	<b>Conventional Desulfurization</b>	<b>Severe Desulfurization</b>	<b>Mild Isocracking</b>
% HDS	90.0	99.8	99.6
Sulfur, wt% of feed	2.67	2.67	2.57
Nitrogen, ppm of feed	720	720	617
Gravity, °API of feed	22.6	22.6	23.0
Light Isomate Product			
Sulfur, wt%	0.07	0.002	0.005
Nitrogen, ppm	18	20	20
Gravity, °API	30.9	37.8	34.0
Heavy Isomate Product			
Gravity, °API	27.1	29.2	30.7
Sulfur, wt%	0.26	0.009	0.013
Nitrogen, ppm	400	60	47

Source: McKetta (1992).

### 5.5 Population

Data regarding the population of single-stage or two-stage hydrocracking (including isocracking) processes are identified from Hydrocarbon Processing (November 1998 and November 2000). Worldwide, there are over forty such units currently operating (including revamps of pre-existing processes). Data specific to the U.S. are available for Chevron-designed hydrocracking (Isocracking) units only. Table 5-6 lists Chevron-designed hydrocrackers in operation in the U.S. as of 1991 (McKetta, 1992). The Ferroalloys Association provided the names of facilities that perform all types of single and multi-stage hydrocracking processes. The non-Isocracking facilities are listed in table 5-7.

**Table 5-6. Chevron-Designed Hydrocracking Plants**

<b>Company (as of 1991)</b>	<b>Location</b>	<b>Major Products</b>	<b>Start-up Year</b>	<b>Capacity (BPSD)</b>
Sohio	Ohio	N	1962	12,000
Chevron	Mississippi	N	1963	28,000
Tosco	California	N	1963	22,000
Chevron	California	N/K/F	1966	30,000
Chevron	California	N/K	1966	50,000
Sohio	Ohio	N/F	1966	25,000
Mobil	California	N	1967	16,000
Tenneco	Louisiana	N	1968	16,000
Mobil	Texas	N	1969	29,000
Chevron	California	N/K	1969	50,000
Sohio	Ohio	N/L	1970	20,000
Chevron	Mississippi	N/K	1971	32,000
BP Oil	Pennsylvania	N	1975	20,000
Hawaiian Independent	Hawaii	K	1981	12,000
Chevron	California	L	1984	18,500
Chevron	California	L	1984	12,000
Total Isocracking Capacity				392,500
Total 2000 Hydrocracking Capacity*				1,575,800

Source: Chevron Research Company in McKetta, 1992.

D=diesel, F=FCC feed, G=LPG, K=kerojet, L=lubes, N=naptha

\*For comparison. From U.S. DOE (2000).

Note: In comments from The Ferroalloys Association (September 4, 2001), the commenter provided the names of eight facilities that perform Isocracking. It appears that the facilities identified in this table overlap with the Association's list.

**Table 5-7. Other Single and Multi-Stage Hydrocracking Processes\***

<b>Company</b>	<b>Location</b>	<b>Process Type</b>
Arco	Carson, CA	UOP Unicracking
Arco	Cherry Point, WA	UOP Unicracking
Excel Paralubes	Lake Charles, LA	UOP Unicracking
Equilon	Wilmington, CA	UOP Unicracking
Equilon	Wood River	Shell
Exxon	Baton Rouge, LA	UOP Unicracking
Exxon	Baytown, TX	UOP Unicracking
Exxon	Billings, MT	UOP Unicracking
Tesoro	Kapolei, HI	UOP Unicracking
Tosco	Rodeo, CA	UOP Unicracking
Tosco	Wilmington, CA	UOP Unicracking

\*Information in this table was derived from comments from The Ferroalloys Association (September 4, 2001)

### 5.6 Conclusions

Based on the above information, the following conclusions are reached regarding staged hydrocracking processes:

- Single stage hydrocracking processes offer no H<sub>2</sub>S or NH<sub>3</sub> removal between reactors, while two stage processing employs interstage gas and light products removal. All reactors are fixed bed.
- First stage units conduct hydrotreating functions such as nitrogen and sulfur removal. Second stage units also may conduct sulfur removal, but little to no nitrogen removal. Second stage units are designed for cracking.
- Due to the fact that single-stage units offer no H<sub>2</sub>S or NH<sub>3</sub> removal between reactors, the subsequent cracking reactors must use a catalyst specifically designed to operate in the presence of high contaminant levels such as high activity or nitrogen/NH<sub>3</sub> resistant zeolite catalysts.
- Complete, or near complete, conversion of the feed can be achieved through the addition of a recycle stream which passes the uncracked material repeatedly over the cracking catalyst to the point of extinction.

- High sulfur and nitrogen removal rates are identified. Although sources indicate most nitrogen is removed in the first stage of a multi stage process, data are unavailable to confirm this. Sources also indicate that sulfur reduction occurs in both stages, although again stage specific removal rates were not found in the literature.

## 6. Lube Oil Processes

There are five basic steps to manufacturing lube oil base stocks from crude oil: distillation, deasphalting, refining, dewaxing, and finishing. The first two steps prepare the feedstocks, while hydroprocessing may take place in any of the following three steps. Collectively, these five steps serve the purpose of improving the viscosity index, quality, temperature properties, color, and stability of the lube base stock. Refining is achieved through the use of solvents or hydrogen. Dewaxing processes use either solvents or catalysts. Clay or hydrogen is used for product finishing. The most common lube oil manufacturing process route is that which consists of solvent refining, solvent dewaxing, and hydrogen finishing (McKetta, 1992). Licensed lube oil processes include:

- Shell Hybrid. Licensed by Shell Global Solutions International B.V.
- Yukong UCO Lube Process. Licensed by Washington Group International, Petroleum and Chemicals Technology Center, under exclusive arrangement with SK Corporation.
- Mobil Selective Dewaxing (MSDW) Process. Licensed by Mobil.

These are discussed in the following sections, but should not be assumed to be a comprehensive listing of all technologies.

### 6.1 Hybrid

The Shell Hybrid base oil process is a combination of solvent extraction and one-stage hydroprocessing. It can be installed as a revamp to an existing solvent extraction lube oil plants in order to increase capacity (by up to 60 percent). Process feeds can be derived from a wider range of crudes than those feeds used with solvent extraction alone. Yields and capacity are less sensitive to feedstock when solvent extraction is used in conjunction with hydroprocessing (Hydrocarbon Processing, November 2000).

The Hybrid base oil process consists of two separate upgrading units, a solvent extractor and a one-stage hydroprocessor. The types of solvent extraction and hydroprocessing depend upon the feedstock and manufacturing objectives. Hydrotreating within the process yields higher quantities of low-sulfur, low-pour-point gas oil byproducts which reduces the quantity of low-value byproducts produced (Hydrocarbon Processing, November 2000).

### 6.2 Yukong UCO Lube Process

The purpose of the Yukong UCO Lube Process is to produce higher quality lube base stocks from unconverted oil (UCO). UCO from a fuels hydrocacker is used as feed to the

Yukong UCO Lube process due to its characteristically low sulfur, oxygen, and metals content. This feed requirement is due to the deactivation effect these impurities have on the lube process catalyst. The pilot plant used in conjunction with the development of the Yukong UCO Lube Process consists of three sections: feed preparation, reaction, and product separation. The feed preparation section is a vacuum distillation column. The reaction section consists of two independently controlled and operated units. The first reactor is for the purpose of hydrodewaxing (HDW) and the second is for hydrotreating (HDT). Both reactors have operating conditions of 0 to 205 atm or higher. The product separation section consists of two columns. The first column removes light material by fractionation for the purpose of feeding the bottom to a vacuum distillation column. The bottom stream of the second column is the final lube base oil product (Andre', 1996).

### 6.3 Mobil Selective Dewaxing Process

Catalytic dewaxing is a shape selective kinetic process which selectively cracks and/or isomerizes wax molecules. The Mobil Selective Dewaxing Process (MSDW) provides improved lube yields and viscosity index and requires either severely hydrotreated or hydrocracked feeds. The process is based on a catalyst that combines isomerization and selective cracking resulting in dewaxed oil yield and the viscosity index being equivalent or higher than for solvent dewaxing. Noble metals can be incorporated into the catalyst due to the use of "clean" (*i.e.*, low in sulfur, nitrogen, and coke precursors) feedstocks. Increased catalyst activity and cycle length are realized with the addition of the metal component due to its reduction affect on the rate of coke formation. Operating pressures vary between 27 to 205 atm. Higher operating pressures result in increased cycle length and higher yield and viscosity index. The MSDW process can handle light and heavy neutral hydrorefined feedstocks (Baker, 1995).

### 6.4 Conclusions

Based on the information presented in this section, the following conclusions can be made in regard to lube oil hydroprocessing:

- Lube oil hydroprocessing units require a "clean" feed. Such feeds have low sulfur, nitrogen, and metals concentrations. Typically these feeds are the products of fuel hydrocracking units.
- Lube oil hydroprocessing catalysts can incorporate noble metals witch enhance the quality of the product but are also sensitive to feed impurities.
- The above mentioned licensed process units use hydroprocessing to increase the quality of the lube stock produced. Other licensed process units not identified from the literature may have similar characteristics. Not all lube oil processes use hydroprocessing.
- Using hydroprocessing in conjunction with traditional solvent extraction methods of dewaxing allows for processing of a wider range of feedstocks than would be possible with solvent extraction alone.

## 7. Recycling Spent Catalysts

EPA wants to encourage recycling and reclamation of hazardous wastes, as well as to conserve resources that would alternatively be used if hazardous waste recycling did not occur. This section provides a summary of information currently available to EPA regarding the quantities of spent catalyst managed by different management practices, and the costs of these management practices, both prior to and following the promulgation of the K171 and K172 listings. Moreover, this section assesses trends in activities, or factors affecting management alternatives. For spent catalysts, the principal waste management options are recycling practices and disposal practices. EPA hopes to work with stakeholders to identify methods of increasing recycling for K171 and K172 waste streams. Section 7.1 presents EPA's waste management data concerning the quantities of K171 and K172 wastes being landfilled or recycled. Section 7.2 provides EPA's current cost data for various waste management practices or steps, including recycling. Section 7.3 discusses the recycling trends shown in the data.

### 7.1 Quantity Data

EPA initially collected waste management data for spent hydrotreating and hydrorefining catalysts in its 1992 RCRA §3007 survey (EPA, 1995). These data were presented in EPA's background document for the 1998 final rule, and represent management practices prior to implementation of the listings.

The K171 and K172 listings became effective in February 1999 (i.e., six months after the publication date of August 6, 1998). Therefore, most refineries generating spent hydrotreating and hydrorefining catalysts in 1999 were required to manage them as hazardous wastes, consistent with the Subtitle C program and land disposal restrictions. Such data subsequently were recorded in the 1999 Biennial Reporting System (BRS). The BRS provides a good way to assess the generation and management of K171 and K172, and to see how the quantities generated and the management methods compare to data collected by EPA in 1992, prior to the listing.

Table 7-1 compares the quantities of spent hydrotreating and hydrorefining catalysts generated by refineries in 1992 and 1999. Observations include the following:

- There was a 25 percent increase in the total quantity of K171/K172 (combined) generated from 1992 to 1999.
- The quantities of K171 and K172 generated in 1999 have almost a reverse profile from that generated 1992. In 1992, the quantity of K172 was much larger than K171, while in 1999 the opposite was true.
- A few refineries (20 percent of the quantity) identify the waste as either ignitable (D001) or reactive (D003) in addition to the listed hazardous waste codes (see table footnote).

**Table 7-1. K171/K172 Waste Generation Data in 1992/1999**

Waste Type	Number of Refineries Generating		Waste Quantity Generated (short tons)	
	1999	1992	1999 <sup>1</sup>	1992
Total	106 <sup>2</sup>	—	34,445	26,701
K171	95	92	20,841	6,204
K172	13	38	7,067	20,497
Both K171 and K172 <sup>3</sup>	7	0	6,537	0

Data are limited to wastes generated by petroleum refineries. Additional waste quantities ‘generated’ by facilities outside the refining industry (e.g., waste treatment and disposal) are not included in this table.

<sup>1</sup>Eighteen refineries reported generating a total of 6,787 tons (20 percent of the total) of hazardous waste coded as D001/D003 in 1999, in addition to the codes reported in the table. This data is not included in the table because it would ‘double count’ the quantities already presented.

<sup>2</sup>Not equal to sum of the numbers below, because some refineries generate more than one type of waste.

<sup>3</sup>Refers to waste identified as ‘K171 and K172,’ as one waste shipment.

1999 data source: BRS, GM Form.

1992 data source: 1995 EPA Listing Background Document.

Table 7-2 identifies the management practices used in 1992 and 1999 for spent hydrotreating and spent hydrotreating catalysts. The data are illustrated graphically in Figure 7-1. The total quantities given in Table 7-2 for 1999 are slightly different than those in Table 7-1, because slightly different source data were used within BRS for 1999. The quantities in Table 7-2 include only those wastes received directly from refineries. Quantities such as those generated by waste treatment facilities and further managed by waste disposal facilities are not included in these tables. Table 7-2 illustrates the following:

- Most spent catalyst hazardous waste is listed as K171 rather than as K172. This is consistent with Table 7-1.
- The vast majority of listed waste received by incineration and reclamation/regeneration facilities is K171. Conversely the majority of listed waste received by stabilization/ landfill facilities is K172.
- Incineration, a negligible management technique in 1992, accounted for a small but significant quantity of waste management in 1999.
- Both the total quantity, and the percentage of total volume of spent catalyst, landfilled between 1992 and 1999 increased.
- Recycling/reclamation was still a significant management technique in 1999, although the percentage of spent catalyst managed in this manner decreased from 82% in 1992 to 55% in 1999.

**Table 7-2. Waste Management Data for Spent Catalyst (1992/1999)**

Waste Code	Quantity Managed (short tons)							
	Reclamation/Regeneration		Stabilization/Landfill		Other		Total	
	1992	1999	1992	1999	1992	1999	1992	1999
K171	4,701	15,634	1,165	1,692	339	1,686	6,205	19,012
K172	16,926	879	3,571	8,291	0	57	20,497	9,227
Both K171 and K172	--	573	--	1,343	--	724	--	2,640
Total	21,850	17,086	4,805	11,326	47	2,467	26,702	30,879

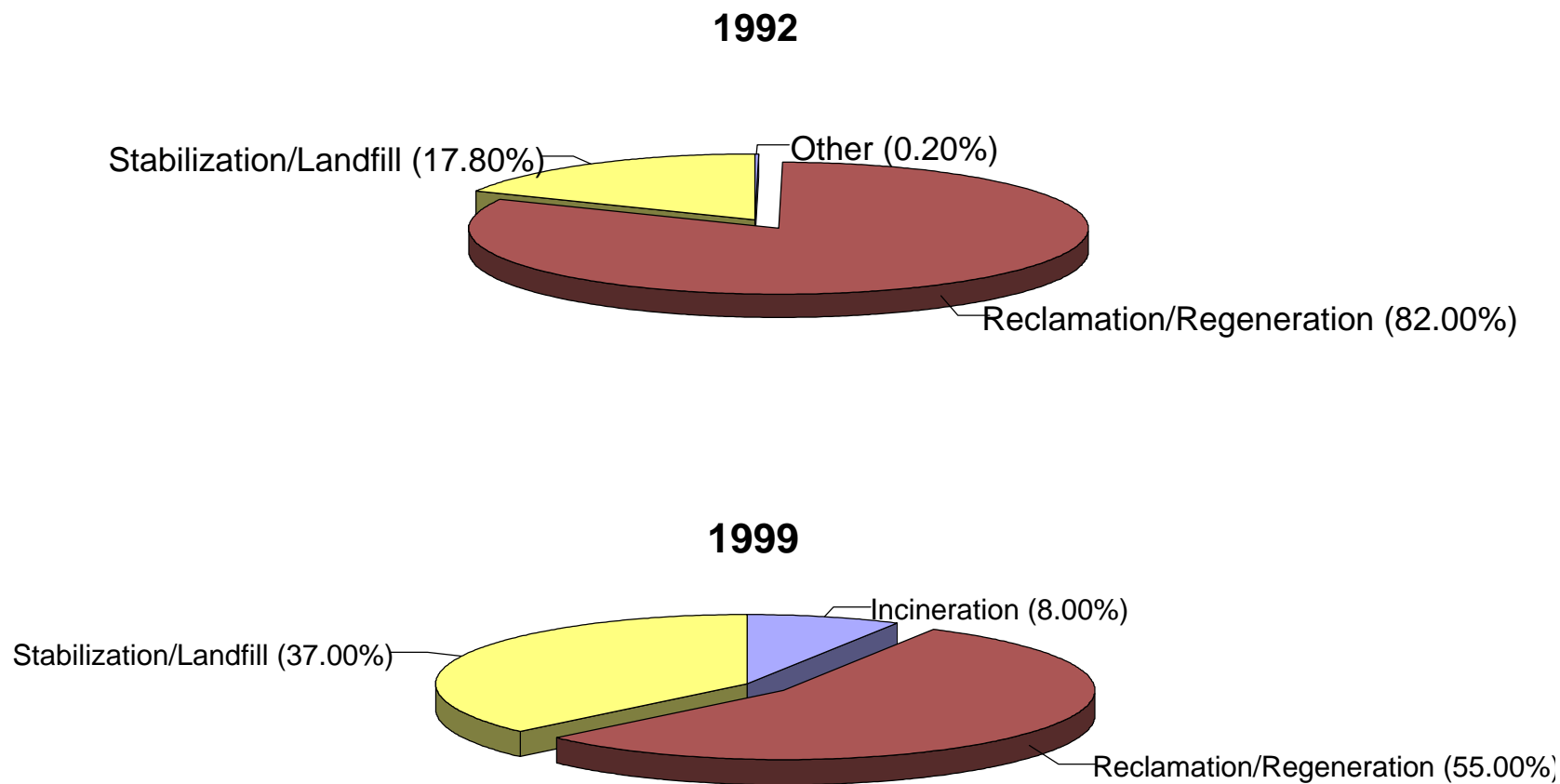
Data are limited to wastes received from petroleum refineries. Additional waste quantities “received” from facilities outside the refining industry (e.g., waste treatment and disposal) are not included in this table.

Ten facilities reported receiving a total of 5,912 tons (19 percent of the total) of hazardous waste coded as D001/D003 in 1999, in addition to the codes reported in the table. This data is not included in the table because it would “double count” the quantities already presented.

1999 data source: BRS, WR Form.

1992 data source: 1995 EPA Listing Background Document.

**Figure 7-1. Waste Management Destinations for Spent Catalyst (1992 vs. 1999)**



## 7.2 Cost Data

For the petroleum listing final rule, EPA performed an Economic Analysis of the costs of managing catalyst wastes.<sup>4</sup> Table 7-3 identifies the costs of reclamation versus treatment and disposal prior to and following the listing. There were many management options envisioned in the Economic Analysis, but Subtitle C disposal and recycling represent some of the most common alternatives. See Section 8.3 for further discussion.

**Table 7-3. Unit Costs for Common Management Methods**

<b>Management Practice</b>	<b>EPA Data<sup>1</sup></b>	<b>API Estimates<sup>2</sup></b>
Reclamation/ regeneration	Pre-listing: \$725/MT  Post-listing: Assumed 5 percent increase in price due to Subtitle C storage, transportation, and management costs.	Pre-listing: \$250/ton  Post-listing: \$500-800/ton
LDR treatment and Subtitle C disposal	Pre-listing: Off-Site Subtitle C disposal: \$233/MT (no LDR treatment occurred)  Post-listing: LDR Treatment: \$240/MT Off-Site Subtitle C Disposal: \$233/MT	Pre-listing: \$130/ton  Post-listing: \$200/ton

1. The EPA figures are provided in 1992 dollars. Source: Cost and Economic Impact Analysis of Listing Hazardous Wastes from the Petroleum Refining Industry. September 21, 1995.

2. API Estimates were provided in public comments to the July 5, 2001 *Federal Register* Notice, dated September 4, 2001. The estimates are drawn from API's primary comments as well as comments to the 1998 final rule. The estimates assume a volume of 900 tons of spent catalyst.

## 7.3 Recycling Trends Analysis

EPA data and API data and information indicate that recycling is significantly lower than the recycling rate prior to the listing decision. As shown in section 7.1, the data collected by the agency can be used to compare recycling rates from 1992 to 1999 (the year in which the listing came into effect). EPA's data indicates that recycling rates decreased from 82 percent to 55 percent. API also indicated in its comments that recycling rates are down throughout the industry, although the comment did not provide specific rates or data to support the information.

There are many reasons that the recycling rate may have dropped so dramatically. The drop could be attributable to the change in recycling costs after the listing came into effect (illustrated in section 7.2). EPA has not collected data on recycling costs after the listings went

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<sup>4</sup>Cost and Economic Impact Analysis of Listing Hazardous Wastes from the Petroleum Refining Industry. September 21, 1995.

into effect. In the economic analysis to the final rule, EPA estimated a five percent increase in costs due to the increased cost of transporting and storing hazardous wastes. The cost of storage was not considered a significant issue because most recycling facilities had acquired a Subtitle C permit pre-listing for the storage of catalysts that exhibit a characteristic. API's estimates for the cost of recycling appear to be inconsistent with the economic data collected by the Agency. In particular, the EPA estimates for the cost of recycling prior to the 1998 final rule are almost three times the estimates provided by API. Since the post-listing estimates are relatively close to one another, the increase in price is far more dramatic from the perspective of the API estimates, but may also better explain the reason for the decrease in recycling rates.

The cost increase may be at least partially explained by a depressed vanadium market. In the past, the value of recycled vanadium allowed the recycling facilities to pass back the benefits to refineries by reducing costs. However, it appears that there is substantial variation in the market price for vanadium. USGS data for vanadium identifies that annual average prices between 1994 and 1997 were roughly \$3 to \$4 per pound. Between 1999 and 2001, annual average prices were only \$1 to \$2 per pound.<sup>5</sup>

The rate of recycling may also be down due to changes in marketplace behavior. For example, comments to the 1998 rule indicated that catalysts may have been recycled to avoid the environmental liability of long-term disposal (API comment to 1998 final rule, p. 102). Prior to the 1998 final rule, refineries recycled because they did not want to be liable for Subtitle D landfilling of what could become hazardous waste. A significant portion of the spent catalyst was handled as characteristic (ignitable) waste. After the rule became final, liability from disposal was no longer a factor (since Subtitle C disposal was now required). Moreover, liability concerns from recycling mismanagement of hazardous residuals may have increased. Both liability factors lead to a potential for a higher percentage of landfilling compared to recycling.

Prior to the 1998 final rule, commenters representing petroleum refineries argued that EPA should promulgate a conditional exemption from the hazardous waste listings for spent hydrotreating catalysts and spent hydrorefining catalysts that are recycled. Commenters argued that a conditional exemption from the hazardous waste listing would encourage more recycling of spent catalysts. In the 1998 final rule, EPA had concerns regarding potential risks from management, such as improper storage (63 FR 42158), and thus stated that the waste is not a good candidate for a conditional listing. These potential risks included risks beyond those necessarily associated with landfill disposal, including pyrophoric properties and significant levels of benzene and arsenic (all of which may pose risks via pathways other than groundwater exposure, including risks from improper storage or other handling, and risks from uncontrolled air emissions from thermal treatment).

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<sup>5</sup> U.S. Geological Survey data for vanadium. Mineral Commodity Summaries.

## 8. Discussion

### 8.1 Characteristics of Hydroprocessing Units

General characteristics of hydroprocessing technologies, including hydrotreating and hydrocracking, were discussed in Section 2. Hydrocracking is a catalytic petroleum refining process that converts heavy, high boiling feedstock molecules to smaller, lower boiling products through carbon-carbon bond breaking accompanied by simultaneous or sequential hydrogenation (Scherzer, 1996, p.1). Hydrotreating is a process whose primary purpose is to saturate olefins and/or reduce sulfur and/or nitrogen content (and not to change the boiling range) by reacting the feed with hydrogen (Gary, 1994, p. 187). Hydrorefining, while present in EPA's regulatory definition of K172, is a term generally not used in literature and instead is encompassed within "hydrotreating." In virtually all cases presented in this report, hydrocracking is accompanied with or preceded by hydrotreating reactions. This is due to the deactivating effect that sulfur and nitrogen compounds have on hydrocracking catalysts (Scherzer, 1996, p.174).

The feedstocks used in the hydrocracking process contain sulfur, nitrogen, and, in the case of resid feedstocks, metals such as nickel and vanadium. The function of the hydrocracking catalyst is to promote hydrocracking reactions with acid sites and promote hydrogenation with metal sites (McKetta, 1992, p.601). The composition of the catalyst is dependent upon the feed material, specific process, and desired product of the process. Most hydrocracking catalysts are a crystalline mixture of silica-alumina with small amounts of rare earths contained within the crystal lattice. The silica-alumina performs the cracking while the rare earths promote hydrogenation. The most commonly used rare earths are platinum, palladium, tungsten, and nickel (Gary, 1994, p. 156-157). Acidic support consists of: amorphous oxides (*e.g.*, silica-alumina), a crystalline zeolite (mostly modified Y zeolite) plus binder (*e.g.*, alumina), or a mixture of crystalline zeolite and amorphous oxides. Cracking and isomerization reactions take place on the acidic support. Metals can be noble metals (palladium, platinum), or nonnoble metal sulfides from group VIA (molybdenum, tungsten) and group VIIA (cobalt, nickel) (Scherzer, 1996, p.13-15).

In the hydrotreating process, sulfur-containing hydrocarbons are converted into low-sulfur liquids and hydrogen sulfide. Nitrogen and oxygen compounds also are dissociated by hydrotreating. This process is operated under high temperatures and pressures. The purpose of the hydrotreating catalyst is to promote hydrogenation reactions using metal sites (McKetta, 1992, pp. 81, 601). Hydrogenation is the addition of hydrogen to a carbon-carbon double bond (Gary, 1994, p. 150). Typical catalyst compositions include cobalt and molybdenum oxides on alumina, nickel oxide, nickel thiomolybdate, tungsten and nickel sulfides, and vanadium oxide. CoMo catalysts are selective for sulfur removal and NiMo catalysts are selective for nitrogen removal (Gary, 1994, p.189).

### 8.2 Performance Summary of Hydroprocessing Units

Throughout this report there are many instances where reduction in sulfur, nitrogen, and metals content are demonstrated between feed and product. This type of reduction is an integral part of hydroprocessing, not only because of the demand for "cleaner" fuels but also because of

the harmful effect that sulfur and nitrogen heteroatoms and metals such as vanadium and nickel have on expensive hydrocracking catalysts. Most hydrocracking processes employ both hydrotreating and hydrocracking steps for this reason. The significant sulfur, nitrogen, and metals content reductions are characteristics of hydrotreating.

The following tables reiterate the information and examples previously given in the report for specific hydroprocessing units. Here, however, the specific reductions are organized according to property (sulfur, nitrogen, metals). Conclusions from these tables are discussed in Section 8.3. Table 8-1 presents data on sulfur, Table 8-2 presents data for nitrogen, and Table 8-3 presents data for metals. Data are presented as available for these constituents in feed, products, and overall reductions. While Section 2 discussed other characteristics of hydrotreating (*e.g.*, olefin hydrogenation), operating data were typically unavailable to quantitatively demonstrate such processes within these units.

Table 8-4 presents information regarding the conversion of various processes discussed in this report. Conversion is the reduction of the amount of material boiling above a certain temperature. Cuts, or fractions are characterized by their boiling ranges (*i.e.*, by an initial boiling point and endpoint). The initial boiling point and endpoint of a fraction increases with the average molecular weight of the fraction, as does the sulfur content (Scherzer, 1996, p. 2). Therefore, a conversion of 80 percent means that 80 percent of the feed is broken down into fractions with lower, generally more desirable, molecular weights and boiling ranges, relative to the feed or a heavy product fraction.

**Table 8-1. Sulfur Reduction in Named Processes**

Process Name	Sulfur Content in Typical Feed	Sulfur Reduction, or Content in Product	Reference
<b>Ebullating Bed</b>			
H-Oil	—	55-92 wt% reduction	Colyar, 1997
H-Oil	—	84-91 wt%	Hydrocarbon Processing, 1998
H-Oil	6.0 wt%	88.0 - 90.1 % reduction	Nongbri, 1992
H-Oil	2.7 wt %	0.06 - 1.55 wt % (depending on product)	Schrezer, 1996
H-Oil	5.33 wt %	0.02 - 1.04 wt % (depending on product)	Wisdom, 1997
H-Oil	4.71 wt%	—	Wisdom, 1997
LC-Fining	3.9 - 4.97 wt%	60-90 wt% reduction	Hydrocarbon Processing, 1998

**Table 8-1. Sulfur Reduction in Named Processes**

<b>Process Name</b>	<b>Sulfur Content in Typical Feed</b>	<b>Sulfur Reduction, or Content in Product</b>	<b>Reference</b>
T-Star	—	93-99 wt% reduction	Hydrocarbon Processing, 2000
T-Star	2.8 wt %	91.7 wt% reduction, < 70-1,000 ppmw (depending on product)	Johns, 1993
T-Star	1.93 wt %	97 wt% reduction	Nongbri, 1996
T-Star (mild hydrocracking mode)	2.10	98 wt% reduction	Nongbri, 1996
<b>Mild Hydrocracking</b>			
Typical	27,000 ppmw	300 to < 1,000 ppmw (depending on product)	Marion, 1998
MHUG	10,000 ppmw (VGO)	9 - 19 ppmw (depending on product)	Chen, 1999
MHUG	10,400 (LCO)	16 ppmw (diesel)	Chen, 1999
<b>Stage Hydrocracking</b>			
IFP Hydrocracking Process	31,700 ppm (HVGO)	<10 - <20 ppm (depending on product)	Hydrocarbon Processing, 1998
MAKFining	29,000 ppm (VGO)	<50 ppm (diesel)	Hydrocarbon Processing, 1998
Isocracking	25,700 ppm	50 to 130 ppm (depending on product)	McKetta, 1992
<b>Lube Oil</b>	No data		

**Table 8-2. Nitrogen Reduction in Named Processes**

<b>Process Name</b>	<b>Nitrogen Content in Feed</b>	<b>Nitrogen Reduction/Content in Product</b>	<b>Reference</b>
<b>Ebullating Bed</b>			
H-Oil	—	25-50 wt% reduction	Colyar, 1997

**Table 8-2. Nitrogen Reduction in Named Processes**

<b>Process Name</b>	<b>Nitrogen Content in Feed</b>	<b>Nitrogen Reduction/Content in Product</b>	<b>Reference</b>
H-Oil	4,800 ppmw	57.3 - 65.7 % reduction	Nongbri, 1992
T-Star	1,328 ppmw	80 wt % reduction 3-766 ppmw (depending on product)	Johns, 1993
T-Star	1,820 ppmw	78 wt % reduction	Nongbri, 1996
T-Star (mild hydrocracking mode)	819 ppmw	94 wt % reduction	Nongbri, 1996
<b>Mild Hydrocracking</b>			
Typical	800 ppmw	—	Marion, 1998
MHUG	2,400 ppmw (VGO)	<0.5 - 6 ppmw (depending on product)	Chen, 1999
MHUG	446 (LCO)	<0.5 - 1.4 ppmw (depending on product)	Chen, 1999
<b>Stage Hydrocracking</b>			
IFP Hydrocracking Process	853 ppm (HVGO)	<5 ppm	Hydrocarbon Processing, 1998
MAKFining	900 ppm	—	Hydrocarbon Processing, 1998
Isocracking	617 ppm	20–47 ppm (depending on product)	McKetta, 1992
<b>Lube Oil</b>	No data		

**Table 8-3. Metals Reduction in Named Processes**

<b>Process Name</b>	<b>Metals Content in Feed</b>	<b>Metals Reduction / Content in Product</b>	<b>Reference</b>
<b>Ebullating Bed</b>			
H-Oil	—	65-90 wt% reduction	Colyar, 1997

**Table 8-3. Metals Reduction in Named Processes**

<b>Process Name</b>	<b>Metals Content in Feed</b>	<b>Metals Reduction / Content in Product</b>	<b>Reference</b>
H-Oil	Nickel: 64 ppmw Vanadium: 205 ppmw	Ni: 78.4 - 81.2 % reduction V: 88.4- 91.4 % reduction	Nongbri, 1992
H-Oil	Nickel + Vanadium 221 ppmw	—	Wisdom, 1997
H-Oil	Nickel + Vanadium 707 ppmw	—	Wisdom, 1997
LC-Fining	Nickel: 18-39 ppmw Vanadium: 65-142 ppmw	50-98 wt% reduction	Hydrocarbon Processing, 1998
T-Star	Nickel: 1.6 ppmw Vanadium: 4.4 ppmw	—	Nongbri, 1996
T-Star	Nickel: <5 ppmw Vanadium: <5 ppmw	—	Nongbri, 1996
<b>Mild Hydrocracking</b>			
Typical	Nickel: 2.5 ppm Vanadium: 16 ppm	—	Environment Technology Center, 1996 - 2000
<b>Stage Hydrocracking</b>	No data		
<b>Lube Oil</b>	No data		

**Table 8-4. Feed Conversions in Named Processes**

<b>Process Name</b>	<b>Type of Feed</b>	<b>Percent Conversion</b>	<b>Reference</b>
<b>Ebullating Bed</b>			
H-Oil	Typical Vacuum Residue	45 - 90 vol%	Colyar, 1997
H-Oil	Arabian Medium Vacuum Resid	65 - 90	Hydrocarbon Processing, 1998
H-Oil	Arabian Heavy Resid	65 - 85	Nongbri, 1992

**Table 8-4. Feed Conversions in Named Processes**

<b>Process Name</b>	<b>Type of Feed</b>	<b>Percent Conversion</b>	<b>Reference</b>
H-Oil	Russian Vacuum Resid	68 vol%	Colyar, 1997
H-Oil	Arabian Crude	70 - 90 vol%	Scherzer, 1996
H-Oil	Arabian Light/Heavy Vacuum Residue	65 - 85 vol%	Wisdom, 1997
H-Oil	Isthmus / Maya Blend	65 - 85 vol%	Wisdom, 1997
LC-Fining	—	40-97 vol%	Hydrocarbon Processing, 1998
T-Star	—	20-60 vol%	Hydrocarbon Processing, 2000
T-Star	—	9 vol%	Johns, 1993
T-Star	Vacuum Gas Oil	30	Nongbri, 1996
T-Star	Vacuum Gas Oil	55	Nongbri, 1996
<b>Mild Hydrocracking</b>			
Typical	Arabian Light	30 wt%	Marion, 1998
MHUG	FCC Feedstock Vacuum Gas Oil	35	Chen, 1999
<b>Stage Hydrocracking</b>			
Typical Single or Two-Stage	Typical Feed ( <i>e.g.</i> , VGO)	70 - 100 wt%	Scherzer, 1996
MAKFining	50/50 Arabian Light/Heavy Blend	50 - 70	Hydrocarbon Processing, November 1998
<b>Lube Oil</b>	No data		

### 8.3 Conclusions

This section serves as a summary of the information presented in this report to identify key characteristics of hydrotreating and hydrocracking processes. It will show the property conversion/reduction ranges and types of catalysts used and their purposes for the four types of

hydroprocessing processes detailed in this report: ebullated bed, mild hydrocracking, single and multi-stage hydrocracking, and lube oil hydroprocessing processes.

### *8.3.1 Ebullated Bed*

The three licensed ebullating bed processes discussed in Section 3 are H-Oil, LC-Fining, and T-Star. These processes are capable of processing very heavy feeds such as VGO or vacuum residue that have not been pretreated prior to being fed to the ebullating bed reactor. Feed conversion for such processes range from 30 to 90 percent depending on process conditions. Feedstock sulfur content reduction as high as 98 percent can be achieved in ebullating bed (dual purpose) reactors depending upon the desired conversion level of the process. Significant nitrogen feed content reduction of up to 94 wt percent is possible with a more typical reduction being about 80 wt percent. Feedstock metals reduction also is achieved in ebullating bed processes. Nickel feed content reduction is on the order of 80 percent and vanadium feed content reduction is about 90 percent. These processes use catalysts with metals removal, hydrotreating, and cracking activities (Gary, 1994, p. 178). The information collected regarding catalyst purpose and activity from Section 2 shows that significant sulfur and nitrogen reductions are characteristic of hydrotreating activity while significant feedstock conversion levels are indicative of hydrocracking activity. Based on information presented in Section 2 regarding characteristics of hydrotreating and hydrocracking, the conclusion can be drawn that both hydrotreating and hydrocracking occur in ebullated bed hydroprocessing units. EPA has identified two U.S. refineries with ebullated bed processes.

### *8.3.2 Mild Hydrocracking*

The mild hydrocracking process is used to process heavy feeds such as vacuum gas oil. As in the ebullated bed processes, feeds are not pretreated prior to being fed to the mild hydrocracking unit. Examples of “typical” mild hydrocracking processes and the licensed MHUG process were investigated. Mild hydrocracking operates on a once-through basis using a single fixed bed reactor. Feed conversions for the mild hydrocracking process are on the order of 30 percent. High rates of sulfur and nitrogen reduction are seen for the examples presented in Table 8-1 and 8-2, respectively. No data regarding metals reduction percentages or product metal content was identified. Therefore, EPA can not determine if demetallization takes place, if the process works best with low feed metal feedstocks only, or if metals in the feed pass through to the products. Catalysts used in the mild hydrocracking process perform both the hydrotreating functions of desulfurization/denitrification and the hydrocracking function of feed conversion. These catalysts are mildly acidic. They usually consist of cobalt or nickel oxide combined with molybdenum or tungsten oxide supported on amorphous silica-alumina or mildly acidic zeolite (Scherzer, 1996). The high rates of heteroatom removal realized with the mild hydrocracking process is characteristic of hydrotreating while the significant (30 percent) feed conversion is characteristic of hydrocracking. Given these product conversions/reductions and the type of catalyst(s) used in these types of processes, the conclusion can be drawn that both hydrotreating and hydrocracking occur in the mild hydrocracking process. An estimate of the number of refineries operating mild hydrocracking processes is unavailable.

### *8.3.3. Single- and Multi-Stage Hydrocracking Processes*

Single and multi-stage hydrocracking processes employ one or more reactors in series. The licensed processes discussed in this report include IFP Technology, MAKFining, and the Shell hydrocracking process. Feedstock conversion using this type of process is in the range of 50 - 100 percent depending on process conditions and design. Specific process examples demonstrated very high sulfur and nitrogen feed content reductions. No metals reduction percentages or product content were identified, most likely because metals removal is not a primary function of hydrocracking reactors. The types of catalysts used in this process are dependent upon the number of reactors used. If a single reactor is used, multiple catalysts for hydrodesulfurization, hydrodenitrification, and conversion reactions can be used in a stacked bed arrangement. If multiple reactors are used, the first reactor in the series typically performs a hydrotreatment function and removes sulfur, nitrogen, and other heteroatoms. The following reactors in the series convert the feed to lighter products. The use of different catalysts or multipurpose catalysts for the purpose of sulfur/nitrogen removal and feed conversion is indicative of both hydrotreating and hydrocracking activity. Depending on the configuration of the reactors, the hydrotreating and hydrocracking reactions may occur within the same reactor, or may be located in different reactors. Even in a two-stage process, some degree of sulfur reduction (a characteristic of hydrotreating) may occur in the second, hydrocracking stage.

### *8.3.4 Lube Oil Processes*

Lube oil hydroprocesses require feeds that have low sulfur, nitrogen, and metals concentrations. Typically these feeds have been severely hydrotreated or hydrocracked prior to being fed to the lube oil processing unit. No information on conversion or sulfur/nitrogen/metals removal percentages was identified for specific lube oil process examples.

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